IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application for:	**Art Unit:** 3749
ADA Environmental Solutions, LLC	
First Named Inventor: Johnson, et al.	**Examiner:** Rinehart, Kenneth
Appln. No.: 10/622,677	**Confirmation No.:** 3654
Filing Date: July 18, 2003	**Atty. Docket No.** 3791-13-CON

For: "LOW SULFUR COAL ADDITIVE FOR
IMPROVED FURNACE OPERATION"

* * *

APPELLANTS' BRIEF
(37 CFR § 41.37)

MS Appeal Brief - Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Appellants hereby appeal to the Board of Appeals in response to the nonfinal Office Action mailed on August 15, 2008. A Notice of Appeal was filed on February 13, 2009. The fee set forth in 37 CFR § 41.20(b) has been previously submitted in connection with the Notice of Appeal. Although Appellants believe that no additional fees are due at this time, authorization to charge any necessary fees to Deposit Account No. 19-1970 is hereby given.

A single copy of this Appeal Brief is being submitted pursuant to MPEP §1205.02.

(i) REAL PARTY IN INTEREST.

All right, title, and interest in this application has been assigned by the inventors, Stephen Allen Johnson, John Wurster, and John Philip Comer to ADA Environmental Solutions, LLC. This Assignment is recorded at Reel/Frame 014682/0603.

(ii) RELATED APPEALS AND INTERFERENCES.

There are no related appeals, interferences or judicial proceedings known to Appellant, or the Appellant's legal representative which may be related to, directly affect, be directly affected by, or have a bearing on the Board's decision in the pending appeal.

(iii) STATUS OF CLAIMS.

Claims 24-26, 33-34, 36, 44-66, 68-88, 90-110, 112-132, 134-137, and 139-141 are currently pending. Claims 1-23, 27-32, 35, 37-43, 67, 89, 111, 133, 138, and 142 have been canceled. Accordingly, claims 24-26, 33-34, 36, 44-66, 68-88, 90-110, 112-132, 134-137, and 139-141 are being appealed.

Claims 24-26, 33-34, 36, 44-66, 73, 78-81, 87-88, 95, 100-102, 109-110, 122-124, 131-132, and 140-141 stand rejected under 35 U.S.C.§112, first paragraph.

Claims 24-26, 33-34, 36, 44-53, 55, 56, 61-66, 68-74, 76-77, 82-88, 90-96, 98-99, 104-110, 112-118, 120-121, 126-132, 134-137, and 139-141 stand rejected under 35 U.S.C.§103(a).

The Claims at issue (*i.e.*, Claims 104-145) are set forth in the CLAIMS APPENDIX.

(iv) STATUS OF AMENDMENTS.

All amendments made by Applicants have been entered by the Examiner. The most recent amendments made on October 27, 2008, in response to a non-final Office Action mailed on June 26, 2008, were entered and considered by the Examiner in the final Office Action dated November 17, 2008.

(v) SUMMARY OF CLAIMED SUBJECT MATTER.

The currently pending Independent Claims 24-26, 33-34, 36, 44-66, 68-88, 90-110, 112-132, 134-137,and 139-141 recited in the Claims Appendix hereto, are directed to methods to operate a solid fuel fired boiler (*See* Specification page 1, lines 18-25; Figure 1; page 1, line 24 through page 2, line 19; page 6, lines 6-19; Figure 9; page 14, line 1; page 18, line 10).

The invention addresses a problem that arises when a low sulfur (western) coal is combusted in a wet-bottom or slag-type furnace of the type shown in Fig. 1 (Specification pages 1, line 18, to page 3, line 8, and Figure 1). Such furnaces are designed for high sulfur (eastern) coals, which are disfavored due to sulfur oxide emissions. When low sulfur coals, with low iron and high alkali contents are combusted, the viscosity of the resulting slag is too low, causing less retained bottom ash (or a higher amount of entrained coal and ash particulates in the off gas from combustion) and therefore a higher incidence of stack opacity violations and increased fuel and maintenance costs, less reliable slag tapping, the occurrence of flames in the main furnace, high furnace exit temperatures, and increased convective pass fouling (Specification page 3, lines 10-17). To overcome these problems, the claimed method adds an iron-containing additive, particularly mill scale from steel production and dust from blast furnace gas cleaning equipment. The iron-containing additive acts as a fluxing agent to decrease the ash melting temperature and induce crystal formation in the melt, which effectively provides a higher viscosity slag in the furnace (Specification at pages 6, line 19, to page 7, line 22).

One embodiment, which is the subject of Independent Claim 24, is directed to a method comprising:

(a) introducing a solid fuel into the boiler (item 100), wherein the solid fuel is a coal having a sulfur content of less than about 1.5 wt.% (dry basis of the coal) (Specification page 1, lines 18-25; Figure 1; page 1, line 24 through page 2, line 19; page 6, lines 6-19; page 18, line 10;Figure 9; page 14, line 1; page 18, line 10);

(b) introducing an iron-containing material into the boiler, wherein the iron-containing material is at least one of mill scale from steel production and dust from blast furnace gas cleaning equipment (Specification page 5, line 18 through page 6, line 4; page 6, line 19 through page 7, line 14; page 11, line 8 through page 12, line 19; Figure 9; page 14, line 1; page 18, line 10); and

(c) at least partially combusting the solid fuel to produce an ash slag, wherein, in the at least partially combusting step (Specification page 2, lines 14-15; page 6, lines 4-5 and 15-18; Figures 1, 4-5, 7-8 and page 20, lines 1-21; Figure 9; page 14, line 1; page 18, line 10), at least one of the following is true:

(i) the ash slag has a fluid temperature less than a fluid temperature characteristic of the ash slag produced from combustion of the solid fuel alone (Specification page 19, lines 5-10; page 5, lines 13-17; page 6, lines 19-22; page 7, lines 15-22; page 8, lines 9-10; page 9, lines 14-15; page 20, lines 1-22; Figures 7-8; Figure 9; page 14, line 1; page 18, line 10); and

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(ii) the ash slag has a melting point less than the melting point of a second ash slag produced from the combustion of the solid fuel alone (Specification page 19, lines 5-10; page 5, lines 13-17; page 6, lines 19-22; page 7, lines 15-22; page 8, lines 9-10; page 9, lines 14-15; page 20, lines 1-22; Figures 7-8; Figure 9; page 14, line 1; page 18, line 10).

One embodiment, which is the subject of Independent Claim 68, is directed to a method of operating a solid fuel fired boiler comprising:

(a) introducing a solid fuel into a wet-bottom boiler (item 100), wherein the solid fuel is a low sulfur coal having a sulfur content of less than about 1.5 wt.% (dry basis of the coal) (Specification page 1, lines 18-25; Figure 1; page 1, line 24 through page 2, line 19; page 6, lines 6-19; Figure 9; page 14, line 1; page 18, line 10);

(b) introducing an iron-containing material into the wet-bottom boiler, wherein the iron-containing material is at least one of mill scale from steel production and dust from blast furnace gas cleaning equipment (Specification page 5, line 18 through page 6, line 4; page 6, line 19 through page 7, line 14; page 11, line 8 through page 12, line 19; Figure 9; page 14, line 1; page 18, line 10); and

(c) at least partially combusting the solid fuel to produce an ash slag, wherein at least a portion of the iron-containing material fluxes the ash slag to cause the ash slag to have a melting temperature less than the melting temperature of a second ash slag produced from the combustion of the solid fuel alone (Specification page 19, lines 5-10; page 5, lines 13-17; page 6, lines 19-22; page 7, lines 15-22; page 8, lines 9-10; page 9, lines 14-15; page 20, lines 1-22; Figures 7-8; Figure 9; page 14, line 1; page 18, line 10)

One embodiment, which is the subject of Independent Claim 90, is directed to a method of operating a solid fuel fired boiler comprising:

(a) introducing a solid fuel into a wet-bottom boiler (item 100), the solid fuel comprising a low sulfur coal having a sulfur content of less than about 1.5 wt.% (dry basis of the coal) (Specification page 1, lines 18-25; Figure 1; page 1, line 24 through page 2, line 19; page 6, lines 6-19; Figure 9; page 14, line 1; page 18, line 10);

(b) introducing an iron-containing material into the wet-bottom boiler, wherein the iron-containing material is at least one of mill scale from steel production and dust from blast furnace gas cleaning equipment (Specification page 5, line 18 through page 6, line 4; page 6, line 19 through page 7, line 14; page 11, line 8 through page 12, line 19; Figure 9; page 14, line 1; page 18, line 10); and

(c) at least partially combusting the solid fuel to produce an ash slag, wherein at least a portion of the iron-containing material fluxes the ash slag to cause the ash slag to have a

viscosity in the boiler less than the viscosity in the boiler of a second ash slag produced from the combustion of the solid fuel alone (Specification page 19, lines 5-10; page 5, lines 13-17; page 6, lines 19-22; page 7, lines 15-22; page 8, lines 9-10; page 20, lines 1-22; Figure 9; page 14, line 1; page 18, line 10; page 2, lines 17-19; page 9, lines 13-19; Figures 3 and 7-8; page 15, lines 5-10; page 18, line12 through page 19, line10; page 20, lines 1-20).

One embodiment, which is the subject of Independent Claim 112, is directed to a method of operating a solid fuel fired boiler comprising:

(a) introducing a solid fuel into a wet-bottom boiler, the solid fuel comprising a low sulfur coal having a sulfur content of less than about 1.5 wt.% (dry basis of the coal) (Specification page 1, lines 18-25; Figure 1; page 1, line 24 through page 2, line 19; page 6, lines 6-19; Figure 9; page 14, line 1; page 18, line 10);

(b) introducing an iron-containing material into the wet-bottom boiler, wherein the iron-containing material comprises iron oxides (Specification page 12, lines 7-19; page 4, lines 12-13; page 6, lines 20-22; page 7, lines 1-14; page 11, lines 11-20; Figure 9; page 14, line 1; page 18, line 10); and

(c) at least partially combusting the solid fuel to produce an ash slag, wherein at least a portion of the iron-containing material fluxes the ash slag to cause the ash slag to have a viscosity less than a viscosity of a second ash slag produced from the combustion of the solid fuel alone (Specification page 19, lines 5-10; page 5, lines 13-17; page 6, lines 19-22; page 7, lines 15-22; page 8, lines 9-10; page 20, lines 1-22; Figure 9; page 14, line 1; page 18, line 10; page 2, lines 17-19; page 9, lines 13-19; Figures 3 and 7-8; page 15, lines 5-10; page 18, line12 through page 19, line10; page 20, lines 1-20).

One embodiment, which is the subject of Independent Claim 134 is directed to a method for operating a slag type furnace comprising:

(a) introducing a coal-containing fuel into said slag type furnace, the coal-containing fuel comprising a low sulfur coal having a sulfur content of less than about 1.5 wt.% (dry basis of the coal) (Specification page 1, lines 18-25; Figure 1; page 1, line 24 through page 2, line 19; page 6, lines 6-19; Figure 9; page 14, line 1; page 18, line 10);

(b) introducing an iron-containing additive into the slag type furnace in an amount sufficient to flux the coal-containing fuel (Specification page 19, lines 5-10; page 5, lines 13-17; page 6, lines 19-22; page 7, lines 15-22; page 8, lines 9-10; page 9, lines 14-15; page 20, lines 1-22; Figures 7-8; Figure 9; page 14, line 1; page 18, line 10); and

(c) melting at least a portion of the coal-containing fuel to produce an ash slag, wherein, in the melting step, at least a portion of the iron-containing additive fluxes the ash

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slag to produce a slag layer having a melting point less than a melting point of a second slag layer without the iron-containing additive (Specification page 19, lines 5-10; page 5, lines 13-17; page 6, lines 19-22; page 7, lines 15-22; page 8, lines 9-10; page 9, lines 14-15; page 20, lines 1-22; Figures 7-8; Figure 9; page 14, line 1; page 18, line 10).

Dependent claim 25 requires the ash slag to have a viscosity during the at least partially combusting step that is less than the viscosity of the second ash slag produced from combustion of the solid fuel alone (Specification page 19, lines 5-10; page 5, lines 13-17; page 6, lines 19-22; page 7, lines 15-22; page 8, lines 9-10; page 20, lines 1-22; Figure 9; page 14, line 1; page 18, line 10; page 2, lines 17-19; page 9, lines 13-19; Figures 3 and 7-8; page 15, lines 5-10; page 18, line12 through page 19, line10; page 20, lines 1-20). *See* claims 51, 72, 85, 94 and 116.

Dependent claim 26 requires the ash slag to have a melting point during the at least partially combusting step that is less than the melting point of the second ash slag produced from combustion of the solid fuel alone (Specification page 19, lines 5-10; page 5, lines 13-17; page 6, lines 19-22; page 7, lines 15-22; page 8, lines 9-10; page 9, lines 14-15; page 20, lines 1-22; Figures 7-8; Figure 9; page 14, line 1; page 18, line 10). *See* claims 87, 107, 109, 129, and 131.

Dependent claim 33 requires at least a portion of the iron-containing material to flux the ash slag to produce a second ash slag having at least one characteristic selected from the group consisting of viscosity and melting temperature less than the same characteristic of the second ash slag produced from combustion of the solid fuel alone (Specification page 19, lines 5-10; page 5, lines 13-17; page 6, lines 19-22; page 7, lines 15-22; page 8, lines 9-10; page 20, lines 1-22; Figure 9; page 14, line 1; page 18, line 10; page 2, lines 17-19; page 9, lines 13-19; Figures 3 and 7-8; page 15, lines 5-10; page 18, line12 through page 19, line10; page 20, lines 1-20).

Dependent claim 34 requires a T_{250} temperature at which the ash slag has a viscosity of 250 poise produced from the combustion of the solid fuel and iron-containing material to be at least 100 degrees Fahrenheit lower than the T_{250} temperature of the second ash slag produced from the combustion of the solid fuel alone (Specification page 19, lines 5-10; page 5, lines 13-17; page 6, lines 19-22; page 7, lines 15-22; page 8, lines 9-10; page 20, lines 1-22; Figure 9; page 14, line 1; page 18, line 10; page 2, lines 17-19; page 9, lines 13-19; Figures 3 and 7-8; page 15, lines 5-10; page 18, line12 through page 19, line10; page 20, lines 1-20).

Dependent claim 36 requires the melting point of the second ash slag to be less than 2600 degrees F (Specification Figures 7-8; page 2 lines 14-17; page 20 lines 14-21; page 18, line 10). *See* claims 88, 110, and 132.

Dependent claim 45 requires the fluid temperature to be less than 2600 degrees F (Specification Figures 7-8; page 2 lines 14-17; page 20 lines 14-21; page 18, line 10).

Dependent claim 47 requires the solid fuel to be introduced into a wet-bottom boiler (Specification page 1, lines 18-25; Figure 1; page 1, line 24 through page 2, line 19; page 6, lines 6-19; Figure 9; page 14, line 1; page 18, line 10). *See* claims 140.

Dependent claim 48 requires the solid fuel to comprise a sub-bituminous coal and wherein the solid fuel has a low iron content and a high alkali content (Specification page 3, lines 1-12; page 6, lines 6-10; page 18, line 10). *See* claims 91 and 113.

Dependent claim 49 requires the boiler to be for at least one of steam production and electricity generation and wherein the iron-containing material has a P_{90} size of no more than about 300 microns (Specification page 8, lines 1-3; page 12, lines 3-6; page 1, lines 18-19; page 12, lines 14-17; page 10, lines 1-3; page 18, line 10). *See* claims 70, 92, 114, 136, and 141.

Dependent claim 50 requires the boiler to be a cyclone boiler (Specification page 1, lines 18-25; Figure 1; page 1, line 24 through page 2, line 19; page 6, lines 6-19; Figure 9; page 14, line 1; page 18, line 10). *See* claim 71.

Dependent claim 52 further requires the step reducing the particle size of the solid fuel prior to introducing the solid fuel into the boiler. (Specification page 5, lines 4-10; Figure 1; Figure 9; page 14, line 1; page 18, line 10). *See* claims 73, 95, and 117.

Dependent claim 53 requires the iron-containing material to be mill scale from steel production. (Specification page 12, lines 7-19; page 18, line 10). *See* claims 74, 96, and 118.

Dependent claim 54 requires the iron-containing material to be dust from blast furnace gas cleaning equipment. (Specification page 12, lines 7-19; page 18, line 10). *See* claims 75, 97, and 119.

Dependent claim 55 requires the iron-containing material to comprise at least one of ferrous oxide and ferric iron oxide. (Specification page 12, lines 7-19; page 4, lines 12-13; page 6, lines 20-22; page 7, lines 1-14; page 11, lines 9-20; page 18, line 10). *See* claims 76, 98, and 120.

Dependent claim 56 requires the iron-containing material to comprise magnetite. (Specification page 7, lines 1-14; page 20, lines 1-3; page 18, line 10). *See* claims 77, 99, and 121.

Dependent claim 57 requires the iron-containing material to comprise at least one carbon compound. (Specification page 3, lines 6-8; page 4, lines 12-14; page 12, lines 13-19; page 13, lines 10-13; page 18, line 10). *See* claims 78, 100, and 122.

Dependent claim 58 requires the further step of introducing at least one carbon compound along with the iron-containing material, the at least one carbon compound being one or more of a hydrocarbon, oil, grease, and xanthan gum. (Specification page 3, lines 6-8; page 4, lines 12-14; page 12, lines 13-19; page 13, lines 10-13; page 18, line 10). *See* claims 79, 101, and 123.

Dependent claim 59 requires the boiler to comprise:

a particle size reduction device, wherein the solid fuel is fed to the device;

a burner;

a fuel transfer system communicating with the device and the burner; and

a combustion chamber comprising an enclosure at least partially surrounding the burner and the further step of:

introducing the iron-containing material into at least one of the fuel storage bunker, the fuel transfer system, the cyclone burner, and the combustion chamber. (Specification Figures 1, 4, 5; page 1, lines 24-28; page 2, lines 1-19; page 14, lines 1-22; page 15, lines 1-4; page 16, lines 4-22; page 17, lines 1-20; Figure 9; page 14, line 1; page 18, line 10). *See* claims 80, 102, and 124.

Dependent claim 60 requires the cyclone boiler to comprise:

a fuel storage bunker (items 216 and 304);

a cyclone burner (item 100);

a fuel transfer system (items 232, 240, and 244a,b (Fig. 4) and items 308, 240, and 344a,b (Fig. 5)) communicating with the fuel storage bunker and the cyclone burner; and

a combustion chamber comprising an enclosure at least partially surrounding the burners. (Figures 1, 4, 5; page 1, lines 24-28; page 2, lines 1-19; page 14, lines 1-22; page 15, lines 1-4; page 16, lines 4-22; page 17, lines 1-20; Figure 9; page 14, line 1; page 18, line 10). *See* claims 81, 103, and 125.

Dependent claim 61 requires the iron-containing material to be introduced into the boiler in an amount ranging from about 10 lb/ton of solid fuel to about 50 lb/ton of solid fuel. (Specification page 9, lines 6-7; page 18, line 10). *See* claims 82, 104, and 126.

Dependent claim 62 requires the ash slag to have a total iron concentration of at least about 15 weight percent. (Specification page 15, lines 5-8; page 18, line 10). *See* claims 83, 105, and 127.

Dependent claim 63 requires the iron-containing material to be added to the solid fuel before introducing the solid fuel and the iron-containing material into the boiler. (Specification Figure 4; page 13 lines 19-22; page 14, lines 1-13; Figure 9; page 14, line 1; page 18, line 10).

Dependent claim 64 requires the ash slag to have a viscosity in the boiler less than the viscosity in the boiler of a second ash slag produced from the combustion of the solid fuel alone. (Specification page 19, lines 5-10; page 5, lines 13-17; page 6, lines 19-22; page 7, lines 15-22; page 8, lines 9-10; page 20, lines 1-22; Figure 9; page 14, line 1; page 18, line 10; page 2, lines 17-19; page 9, lines 13-19; Figures 3 and 7-8; page 15, lines 5-10; page 18, line12 through page 19, line10; page 20, lines 1-20).

Dependent claim 65 requires the iron-containing material to be selected from the group consisting of ferrous oxide, ferric oxide, ferrous sulfide, ferric sulfide, and combinations thereof.. (Specification page 12, lines 7-19; page 4, lines 12-13; page 6, lines 20-22; page 7, lines 1-14; page 11, lines 8-20; page 3, lines 6-8; page 18, line 10). *See* claims 86, 108, and 130.

Dependent claim 69 requires the solid fuel to comprise a sub-bituminous coal, wherein the coal has a total iron content of less than about 10 wt.% (dry basis of the ash), and wherein the coal has a calcium content of at least about 15 wt.% (dry basis of the ash). (Specification page 3, lines 1-12; page 6, lines 6-10; page 18, line 10). *See* claims 93, 115, and 139.

Dependent claim 135 requires at least about 33.5% of the iron-containing additive is in the form of ferrous iron and no more than about 66.5% of the iron in the additive is in the form of ferric iron. (Specification page 6, line 19, to page 7, line 14).

(vi) GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL.

Whether Claims 24-26, 33-34, 36, 44-66, 73, 78-81, 87-88, 95, 100-102, 109-110, 122-124, 131-132, and 140-141 comply with 35 U.S.C.§112, first paragraph..

Whether Claims 24-26, 33-34, 36, 44-53, 55-56, 61-66, 68-74, 76-77, 82-88, 90-96, 98-99, 104-110, 112-118, 120-121, 126-132, 134-137,and 139-141 are patentable under 35 U.S.C.§103(a) based on U.S. 1,955,574 to Benner in view of U.S. 4,572,085 to Hepworth.

Whether Claims 57-58, 78-79, 100-101, and 122-123 are patentable under 35 U.S.C.§103(a) based on Benner in view of Hepworth and further in view of U.S. 4,886,521 to Khan.

Whether Claims 59-60, 80-81, 102-103, and 124-125 are patentable under 35 U.S.C.§103(a) based on Benner in view of Hepworth and further in view of U.S. 3,896,746 to Pirsh.

Whether Claims 54, 75, 97, and 119 are patentable under 35 U.S.C.§103(a) based on Benner in view of Hepworth and further in view of U.S. 4,089,507 to Arai, et al.

Whether Claims 68-86, 89-108, 111-130, and 133-139 are patentable under 35 U.S.C.§103(a) based Hepworth in view of U.S. 4,498,402 to Kober, et al.

(vii) ARGUMENT.

Whether claims 24-26, 33-34, 36, 44-66, 73, 78-81, 87-88, 95, 100-102, 109-110, 122-124, 131-132, and 140-141comply with 35 U.S.C.§112, first paragraph.

Before discussing this rejection, it is important to understand the procedural posture of this appeal. The present application was filed to invoke an interference with U.S.6,484,651 to Shepard, Jr., et al. (hereinafter "Shepard") (attached hereto as Exibit "3"). (*See* REQUEST BY APPLICANTS FOR INTERFERENCE PURSUANT TO 37 CFR § 1.607 AND PRELIMINARY AMENDMENT filed July 18, 2003). The objectionable language in the above claims, namely "fluid temperature" was copied from the Shepard patent.

<u>The Examiner bears the burden of establishing a prima facie case why persons skilled in the art would not recognize in the specification disclosure a description of the claimed invention.</u>

Section 112, first paragraph, requires, *inter alia*, that the specification shall contain a written description of the invention, and of the manner and process of making and using it so as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the invention.

The Examiner bears the burden of providing the prima facie case to support the rejection of any application. As stated by the Board of Patent Appeals and Interferences, "the examiner has the initial burden of presenting evidence or reasons why persons skilled in the art would not recognize in [the] specification disclosure a description of the invention defined by the claims. *Ex Parte Sorenson*, 3 USPQ2d 1462, 1463 (B.P.A.I. 1987). The Federal Circuit has stated that "the test for sufficiency of support in a parent application is whether the disclosure of the application relied upon 'reasonably conveys to the artisan that the

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inventor had possession at that time of the later claimed subject matter." *Ralston Purina Co. v. Far-Mar-Co, Inc.,* 772 F.2d 1570, 227 USPQ 177 (Fed. Cir. 1985).

"Upon reply by applicant, . . . [the examiner is required to] fully respond to applicant's rebuttal arguments, and properly treat any further showings submitted by applicant in the reply. When a rejection is maintained, any affidavits relevant to the 35 U.S.C. 112, para. 1, written description requirement, must be thoroughly analyzed and discussed in the next Office action." MPEP§2163.02.

> The specification need not literally recite a claim limitation for a claim to satisfy the requirements of Section 112, first paragraph.

"It is not necessary that the application describe the claim limitations exactly . . . but only so clearly that persons of ordinary skill in the art will recognize from the disclosure that appellants invented processes including those limitations." *In re Wertheim,* 541 F.2d 257, 191 USPQ 90, 96 (C.C.P.A. 1976). "Satisfaction of the 'written description' requirement does not require in heac verba antecedence in the originally filed application." *Staehelin v. Secher,* 24 USPQ2d 1513 (B.P.A.I. 1992). In *Ex parte Parks,* the Board further elaborated:

> Adequate description under the first paragraph of 35 U.S.C. 112 does not require *literal* support for the claimed invention . . . Rather, it is sufficient if the originally-filed disclosure would have conveyed to one having ordinary skill in the art that an appellant had possession of the concept of what is claimed.

Ex parte Parks, 30 USPQ2d 1234 (B.P.A.I. 1994) (emphasis in original).

"While there is no *in haec verba* requirement, newly added claim limitations must be supported in the specification through express, *implicit,* or *inherent* disclosure." MPEP § 2163(I)(B) (emphasis supplied.); *see, e.g.,* MPEP § 2163.02. Morever, the U.S. Court of Appeals for the Federal Circuit in *Eiselstein v. Frank,* 52 F.3d 1035,1038 (Fed. Cir. 1995), reviewed the need for literal support for claim language in the specification and stated:

> In order to determine whether a prior application meets the "written description" requirement with respect to later-filed claims, the prior application need not describe the claimed subject matter in exactly the same terms as used in the claims; it must simply indicate to persons skilled in the art that as of the earlier date the applicant had invented what is now claimed. . . . The test is whether the disclosure of the application relied upon reasonably conveys to a person skilled in the art that the inventor had possession of the claimed subject matter at the time of the earlier filing date (citing *Vas-Cath Inc. v. Mahurkar,* 935 F.2d 1555 (Fed. Cir. 1991) and *Ralston Purina Co. v. Far-Mar-Co, Inc.,* 772 F.2d 1570 (Fed. Cir. 1985)) (internal citations omitted).

By way of illustration, "where no explicit descriptions of a generic invention is to be found in the specification . . . mention of representative compounds may provide an implicit description upon which to base generic claim language." MPEP § 2163(I)(B)(3)(b) (quoting *In re Smith*, 458 F.2d 1389, 1395, 173 USPQ 679, 683 (CCPA 1972). By way of further example, "[b]y disclosing in a patent application a device that inherently performs a function or has a property, operates according to a theory or has an advantage, a patent application necessarily discloses that function, theory or advantage, *even though it says nothing explicit concerning it.*" MPEP § 2163.07(a) (emphasis supplied.) "The application may later be amended to recite the function, theory, or advantage without introducing prohibited new matter." MPEP § 2163.07(a). Inherent properties which do not constitute new matter are those which would be obvious to one skilled in the art from the very nature of the material. *Kennecott v. Kyocera*, 835 F.2d 1149 (Fed. Cir. 1987) (parent application contained adequate support for later filed CIP application's new disclosure of microstructure of ceramic particle where only ceramic particle, and not its microstructure, was described in parent application); Ex *parte Ayers, et al.*, 108 USPQ 444 (POBA 1955); *see, e.g., In re Nathan, et al.*, 328 F.2d 1005, 140 USPQ2d 601 (CCPA 1964) (stereo configuration of a compound is not new matter); *Ex parte Davisson, et al.*, 133 USPQ 400 (POBA 1958) (physical properties of a compound, e.g., optical rotation data and elemental analysis of a disclosed salt, are inherent properties of a compound which can be added to the disclosure after filing); *In re Bowden et al.*, 183 F.2d 115, 86 USPQ 419 (CCPA 1950) (since chemical reactions are frequently unpredictable a specification may be amended at the proper time to supply corrected data subsequently discovered or which is implicit in the application as filed); *Tektronix, Inc. v. United States, et al.*, 165 USPQ 392 (Ct. Cls 1970).

> <u>Claimed subject matter that is not explicitly disclosed in the specification but is disclosed inherently by the specification satisfies Section 112, first paragraph.</u>

Indeed, unstated subject matter satisfies the written description requirement when it is inherently disclosed in the specification. In *In re Smythe*, the court stated:

> *By disclosing in a patent application a device that inherently performs a function, operates according to a theory, or has an advantage, a patent applicant necessarily discloses that function, theory or advantage even though he says nothing concerning it.* The application may later be amended to recite the function, theory or advantage without introducing prohibited new matter.

In re Smythe, 480 F.2d 1376, 178 USPQ 279, 285 (C.C.P.A. 1973) (emphasis supplied).

"To establish inherency, the extrinsic evidence 'must make clear that the missing descriptive matter is necessarily present in the thing described in the reference, and that it would be so recognized by persons of ordinary skill. Inherency, however, may not be established by probabilities or possibilities. The mere fact that a certain thing may result from a given set of circumstances is not sufficient.'" MPEP§2163(I)(B)(3)(b) (quoting *In re Robertson*, 169 F.3d 743, 745, 49 USPQ2d 1949, 1950-51 (Fed. Cir. 1999); *see also* MPEP § 2163.07(a).

Thus, lack of literal support for specific claim terms is not enough to support a rejection under 35 U.S.C. § 112 where one of skill in the art would understand from the disclosure that the inventors had possession of the invention, as claimed, at the time of filing. The declarations of Dr. Bisque (Bisque Declaration) and Dr. Durham (Durham Declaration), both filed July 29, 2004, are evidence of precisely this understanding by one skilled in the relevant art. The Examiner cannot discount the statements of Dr. Bisque by simply stating that the declaration is unpersuasive. The MPEP requires more. The Examiner needs to provide factual reasons explaining why the declaration is not persuasive; that is, why it fails to establish why one of ordinary skill in the art would not reasonably conclude that the inventor had possession of the claimed invention. This the Examiner has failed to do. In fact, the Examiner seems to acknowledge that the declaration is sufficient under the law by stating that the applicant is relying on "inherency" to justify the support of the claims under 35 U.S.C.§112, first paragraph. As noted above, "inherency" establishes compliance with the written description requirement.

Nonetheless, applicant will summarize the contents of the declarations and revisit, in view of the above statement of the law, why the above assertions of the examiner are incorrect.

1. The Examiner's assertion that there is no support in the Specification for the limitations that at least a portion of the iron bearing material fluxes the ash slag to produce an ash slag having a fluid temperature less than the fluid temperature of a second ash slag produced from combustion of the solid fuel alone (Claims 24, 87, 109, 131. and 140-141).

Claim 24 requires at least a portion of the iron bearing material to flux the ash slag to produce an ash slag having a fluid temperature less than the fluid temperature of a second ash slag produced from combustion of the solid fuel alone. Claims 87, 109, and 131 each require, during the combustion of the solid fuel in the presence of the iron-bearing material, that the fluid temperature be less than the fluid temperature of an ash slag produced from combustion

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of the solid fuel alone. Claim 140 requires the boiler to be a slag-tap furnace while claim 141 requires the solid fuel boiler to be used for at least one of steam production and electricity generation.

<u>The claimed invention and U.S. 6,484,651 to Shepard, Jr., et al., (Exhibit "3") use the same reactants under the same reaction conditions in the same reactor to produce the same result, namely the production of a slag having a lower viscosity than a slag produced by combustion of coal alone.</u>

Before responding to the Examiner's rejections, it is important to understand the overlap between the claimed subject matter of Shepard, Jr. et al., and the present application ("the Subject Application") and U.S. Provisional Application 60/213,915, filed June 26, 2000 ("the Provisional Application"), which was incorporated by reference in its entirety in the Subject Application. They each disclose the combustion of the same fuel in the same type of combustion chamber in the presence of the same iron-bearing material additive under the same temperature regime. The fuel is a low sulfur western or eastern coal (*see, e.g.,* Provisional Application at pages 1 and 3; Subject Application at Figure 2, page 2, lines 15-17, page 3, lines 9-12, page 4, lines 3-4 and 7-9, and page 6, lines 4-5; and Shepard Patent at col. 1, line 62-col. 2, line 3, col. 3, lines 26-34 and 55-57and Fuels 3 and 4). The combustion chamber is a "slag tap" or "wet bottom" boiler, such as a cyclone-type boiler (*see, e.g.,* Provisional Application at pages 1-5 and 7-8; Subject Application at Figure 1, page 1, lines 18-26, page 5, lines 16-17, page 6, lines 4-5 and 15-18, and page 18, lines 12-13; and Shepard Patent at col. 2, lines 7-8, col. 4, lines 7-10). The iron-bearing material is mill scale from steel production or dust from blast furnace gas cleaning equipment (*see, e.g.,* Provisional Application at pages 4 and 6; Subject Application at page 12, lines 7-12; and Shepard Patent at col. 4, lines 15-16, col. 8, lines 4-5). The temperature regime is that necessary to combust the solid fuel and melt the ash content of the fuel to form slag. (*see, e.g.,* Provisional Application at pages 1-5 and 7-8; Subject Application at page 2, lines 14-15, page 6, lines 4-5 and lines 15-18, Figures 7-8 and page 20, lines 1-21; and Shepard Patent at col. 2, lines 4-50, col. 5, lines 10-50). In chemistry, it is elementary that the use of the same reactants under the same reaction conditions in the same reactor will produce the same results. (Declaration of Ramon Bisque filed July 29, 2004, at ¶8 (Bisque Declaration attached hereto as Exhibit "1"). This conclusion is consistent with the teachings of Shepard et al., and the subject application. Regarding the results from adding the iron-bearing material, Shepard et al. and the subject application *both* teach that the iron-bearing material fluxes the ash formed from the solid fuel, thereby causing the slag to have a lower viscosity

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than a slag produced by combustion of the coal alone. (Shepard et al. at col. 2, lines 42-47 and lines 58-61; col. 4, lines 22-25; col. 5, line 51-col. 6, line 10; col. 6, lines 52-56; col. 6, line 60-col. 7, line 9; col. 7, lines 43-47; col. 7, lines 57-63; col. 8, lines 7-13; col. 9, lines 21-26; col. 9, lines 56-60; col. 9, line 66-col. 10, line 26; col. 10, lines 52-54; and claim 5; Subject Application at page 18, line 10; page 5, lines 13-17; page 6, lines 19-22; page 7, lines 15-22; page 8, lines 9-10; page 9, lines 14-15; and page 20, lines 1-19).

While applicants use ash melting point to measure the effect of fluxing by the iron-bearing material, Shepard et al. uses ash fluid temperature. For western coals, a reduction in melting temperature necessarily equates to a reduction in ash fluid temperature. (Bisque Declaration at ¶18.)

It is well accepted that fluid temperature of the ash and melting temperature of the ash are equivalent.

One method of determining the different Ash Fusion Temperature ("AFT") characteristics corresponding to the melting temperature of the ash is set forth at pages 20-5 through 20-7 of *"Steam/its generation and use"*, by Babcock & Wilcox (1972) ("the Babcock & Wilcox Article" attached to the Bisque Declaration, in which the AFT properties are determined as part of the ASTM Standard D 1857, *Fusibility of Coal and Coke Ash."*) According to the standard, an ash sample is prepared by burning coal under oxidizing conditions at temperatures of 1470 to 1650°F. The ash is pressed into a mold to form a triangular pyramid cone 0.75 in. in height with a 0.25 in. triangular base. The cone is heated in a furnace at a controlled rate to provide a temperature increase of 15° F per minute. The initial deformation temperature (IT or ID) refers to the temperature at which the tip of the pyramid begins to fuse or show signs of deformation. The softening temperature (ST) is the temperature at which the sample has deformed to a spherical shape where the height of the cone is equal to the width at the base (H=W). The softening temperature is commonly referred to as the fusion temperature. The hemispherical temperature (HT) is the temperature at which the cone has fused down to a hemispherical lump and the height equals one half the width of the base (H=1/2W). The fluid temperature (FT) is the temperature at which the ash cone has *melted* to a nearly flat layer having a specified height. (*See* Bisque Declaration at ¶14.) For the fluid temperature 0.625 the maximum height is 0.0625 in.

It is accepted that the melting point of ash is synonymous with its fluid temperature. *"Steam its generation and use"*, published by Babcock & Wilcox Company (1992), which is

attached hereto as Exhibit "A" to the Bisque Declaration ("Exhibit 1" hereto), states at page 21-6:

> *Fluid Temperature* (FT) – the temperature at which the *ash* cone has *melted* to a nearly flat layer with a maximum height of 0.0625 in. (1.59 mm).

(Emphasis supplied.)

Accordingly, an established, reliable, respected, and objective article has equated ash melting temperature with its fluid temperature.

> Because coal is a mixture of differing minerals and has no distinct melting point, one of ordinary skill in the art would understand ash "melting temperature" (Specification at pages 2, 7, 20 and Abstract) and ash "melting" (Specification at pages 1-2, 6-7, 8, and 20) to refer to ash fluid temperature and ash fluidity, respectively.

Coal Properties, Sampling & Ash Characteristics, by Rod Hatt (which is attached hereto as Exhibit "2") states at page 4:

> Lets [*sic*] start our review with an overview of coal mineralogy and its relationship to coal ash chemistry, melting & slagging properties, and fusion temperature. There are not [*sic*] melting points for coal ash like with ice or other pure compounds, *so when melting is mentioned it is used to represent a decrease in viscosity, rather than a melting point*. When coal ash melts it occurs on both a large scale and a microscopic scale. On the large or bulk scale the ash behaves like a glass. As the temperature of the material increases, its viscosity decreases. At temperatures less than 2000°F, the ash may appear solid, or at least stiff, such as a Tootsie Roll. On a microscopic scale several minerals may have all ready melted, but their concentrations are low when compared to other minerals with higher melting temperatures. As the temperature is increased the ash becomes less viscous or more liquid like. Many reactions are now occurring between the minerals as they melt and become more fluid. As the molten components mix they become more like molten glass. This molten material starts to dissolve the non molten materials like quartz and other minerals. In this way the melting temperature of minerals such as sandstones and shales are lowered by other minerals such as pyrite and limestone.

(Emphasis supplied.)

Based on the statement in the above quotation that one of ordinary skill in the art would understand ash "melting" to represent a decrease in slag viscosity, rather than a distinct melting point, one of ordinary skill would understand ash "melting" to refer to the fluidity of liquefied ash or slag. Thus, one of ordinary skill in the art would understand ash "melting point" to be a temperature at which the ash is fluid, which is also the fluid temperature of the ash.

Regarding ash melting, the Babcox and Wilcox article states at page 20-6:

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The gradual deformation of the ash cone is generally considered to result from differences in melting characteristics of the various ash constituents. As the temperature of the sample is increased, compounds with lowest melting temperature begin to melt, causing the initial deformation. As the temperature continues to increase, more of the compounds melt and the degree of deformation proceeds to the softening and hemispherical stages. *The process continues until the temperature is higher than the melting point of most of the ash constituents and the fluid stage is reached.*

(Emphasis supplied.)

Contrary to the Examiner's assertion that fluid temperature and melting temperature refer to differing properties, the above quotations amply demonstrate that ash fluid temperature *is* equated in the art with ash melting and melting point. (*See* Bisque Declaration at ¶¶13 and 15.)

The Provisional and Subject Applications' use of the terms "flux" and "fluxing agent" conveys to one of ordinary skill in the art that the ash melting temperature, or fluid temperature, is lowered by the iron-bearing additive.

Regarding the AFT-characteristic limitation and the fluxing limitation, namely that the "iron bearing material fluxes the ash slag" in claims 1, 11, 19, 24 and 33 (*see* Office Action at pages 3, 4, 5, and 33), the Provisional and Subject Applications further use the term "flux" and "fluxing agent". (Provisional Application at pages 1, 3-4, and 6-8 and Subject Application at page 5, lines 13-14, page 6, lines 19-22, page 8, lines 10-11).

The Subject and the Provisional Applications each state that the iron-bearing additive fluxes the ash and lowers the melting temperature of the ash. *See e.g.* Provisional Application at page 3, "[i]t is the use of these byproducts of steel and iron manufacturing to *flux the ash* and improve the cyclone operation that is new and unique" and at page 1 "[t]he iron both reduces the melting temperature of the ash, and reduces the slag viscosity at these temperatures due to the presence of iron aluminosillicate crystals in the ash." (Emphasis added). *See e.g.* Subject Application at page 6, lines 19-22, "[t]he iron-containing additive can be in any form and any composition so long as iron is present in sufficient amounts *to flux effectively the feed material*" (emphasis supplied) and page 7, lines 15-18 "...it is believed that the presence of iron in the calcium aluminosilicate slags of western coals causes a decrease in the melting temperature of the ash and crystal formation in the melt when a critical temperature (T_{CV}) is reached." *See also* page 5, lines 13-14 page 8, lines 10-11, Figs. 7-8 and page 20, lines 1-21 of the Subject Application. According to *Hawley's Condensed Chemical Dictionary*, "flux" is defined as "[a] substance that promotes fusing of minerals or

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metals or prevents the formation of oxides." It further defines "fuse" as "[o]f a solid, to *melt*, e.g., a fused salt." (Emphasis supplied.)

The terms "flux" and "fuse" would further suggest to one of ordinary skill in the art that the melting temperature, or fluid temperature, is lowered by the iron-bearing additive disclosed in the Provisional and Subject Applications. (Bisque Declaration at ¶17.)

> The Provisional and Subject Applications' statement that the iron-containing additive lowers the T_{250} of low-sulfur coals conveys to one of ordinary skill in the art that the ash melting temperature, or fluid temperature, of the ash, is lowered by the iron-bearing additive.

The Provisional and Subject Applications further refer to the iron-containing additive lowering the T_{250} (or the temperature at which the ash would have a viscosity of 250 poise and is an important indicator for the minimum temperature at which the slag will flow) for low-sulfur eastern and western coals having low iron and high calcium contents. (Provisional Application at pages 1 and 4-5 and Subject Application at Figure 2, page 2, lines 15-17, page 7, lines 15-18, page 9, lines 14-15, page 19, lines 5-10, Figures 7-8 and page 20, lines 3-21). As shown in Figures 7-8 of the Subject Application, the iron-containing additive lowers the slag viscosity, at temperatures above about 2275°F, compared to a slag when no additive is used. It is inherent that the use of the iron-bearing material to lower the T_{250} of low-sulfur coals having low iron and high calcium contents will lower each of the AFT properties referenced above. (Bisque Declaration at ¶¶18 and 20.) Shepard is directed to combustion of low-sulfur coals having low iron and calcium (lower basicity) (col. 3, lines 19-34; col. 7, lines 42-56; Table I; and Fig. 3) in the presence of the iron-containing additive to reduce viscosity (i.e. AFT characteristics) (col. 7, line 57; col. 8 line 6).

> The Subject and Provisional Applications each state that the iron-bearing additive fluxes the ash and lowers the ash melting temperature, which statements are alternate expressions for and inherently state that the additive lowers the fluid temperature of the AFT characteristics.

As noted above, the Specifications of the Subject and Provisional Applications literally state that the iron-bearing additive fluxes the ash and, as a resulting, lowers the melting temperature of the ash. The fluid temperature is simply an alternate way of defining ash melting temperature and viscosity in the same manner that inches and centimeters are alternative measures for length. As set forth in the Declaration of Dr. Ramon Bisque under 37 CFR § 1.132 ("Bisque Declaration"), attached hereto as Exhibit A, which was submitted

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in the previous Office Action Response of July 29, 2004, the AFT characteristics of initial deformation temperature, softening temperature, hemispherical temperature, and fluid temperature represent a *continuum of constituent melting points* leading to the *ultimate melting temperature of the ash*. (*See* Bisque Declaration at ¶13.) One of ordinary skill in the art would understand the phrase, "melting temperature of the ash" (as used in the Subject and Provisional Applications), to refer to the last (or highest) of a sequence of melting points for differing ash constituents and require that each of the lower melting point constituents have melted. The melting temperature of the ash is therefore synonymous with the fluid temperature. (Bisque Declaration at ¶16.)

<u>Shepard admits that lowering the AFT characteristics in low sulfur coals will necessarily lower the viscosity by adjusting the base-to-acid ratio of the coal.</u>

Shepard, the patent for which Applicants are requesting declaration of an interference, admits that the AFT characteristics are simply a way of measuring the ash viscosity, which is proportional to the melting point or temperature of the ash. Shepard admits that slag tap boilers require ash having low AFT characteristics. (Col. 5, lines 51-58.) It admits that lower sulfur coals generally have ash chemistry and AFT characteristics that are outside the range for which slag tap or cyclone boilers were originally designed because lower sulfur coals have higher AFT characteristics (i.e., higher IDT, ST, HT, and FT) than is desirable for proper ash flow from the bottom of the boiler. (Col. 3, lines 19-34.) It admits that adding suitable amount of iron-bearing material to low sulfur coals with high AFT characteristics will adjust the base-to-acid ratio and ultimately the ash viscosity characteristics to render the low sulfur coals suitable for use in slag tap boilers because the iron-bearing material will adjust the iron content of the slag to more closely resemble that characteristic of coal having low AFT characteristics. (Col. 7, lines 47-56, and col. 9, lines 21-30, and col. 10, lines 21-26.)

Accordingly, based on Shepard, the present application's disclosure that the iron-containing additive lowers the viscosity and melting temperature of low sulfur coal and acts as a fluxing agent would necessarily disclose to one of ordinary skill in the art that the iron-containing additive lowers the fluid temperature of the low sulfur coal.

<u>2.   The Examiner's assertion that there is no support in the Specification for the requirements that the fluid temperature be less than 2600°F (Claims 66, 88, 110, and 132).</u>

Claims 66, 88, 110, and 132 require that the ash fluid temperature be less than 2600°F.

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The Provisional Application at page 1 and the Subject Application at page 2, lines 14-15, disclose that ash, in the absence of the iron-containing additive, melts at normal combustion temperatures ranging from 2600 to 3000°F. The Subject Application and the Provisional Application thereafter each state that the iron-bearing additive fluxes the ash and lowers the melting temperature of the ash. *See e.g.* the Subject Application at page 7, lines 15-18 "...it is believed that the presence of iron in the calcium aluminosilicate slags of western coals causes a decrease in the melting temperature of the ash and crystal formation in the melt when a critical temperature (T_{CV}) is reached." As discussed in the Bisque Declaration at ¶¶13 and 16, the AFT characteristics refer to a continuum of ash component melting points with the last (or highest) of the continuum of melting points being the melting temperature of the ash or AFT characteristic fluid temperature.

From the statements in the Provisional and Subject Applications that the ash, in the absence of the iron-containing additive, melts at temperatures ranging from 2600°F to 3000°F and that the ash melting temperature is reduced by the iron-containing additive, it follows deductively that the melting temperature or the AFT characteristic fluid temperature of the ash is reduced and less than 2600°F.

The Bisque Declaration further states in ¶22 as follows:

> I disagree. The Provisional Application at page 1 and the Subject Application at page 2, lines 14-15, disclose that the ash (from which the molten slag is formed), in cyclone boilers, must be melted at normal combustion temperatures ranging from 2,600 to 3,000°F. Moreover, the Subject Application at page 20 and in Figure 7 shows that the ash/slag is melted at a temperature below 1,900°F.

Thus, the elements of Claims 66, 88, 110, and 132 are described in the specifications of both the Provisional and Subject Applications in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time each of the applications was filed, had possession of the claimed invention.

3. The Examiner's implication that claims 140-141 lack support in the Specification.

The Examiner rejects these claims under Section 112, first paragraph. These claims are supported in the Specification. Support for claim 140 includes page 1, lines 18-25; Figure 1; page 1, line 24 through page 2, line 19; page 6, lines 6-19; Figure 9; page 14, line 1; page 18, line 10. Support for claim 141 includes page 8, lines 1-3; page 12, lines 3-6; page 1, lines 18-19; page 12, lines 14-17; page 10, lines 1-3; page 18, line 10.

4.   The Examiner's requirement of explicit disclosure to comply with the written description requirement is unsupported by the law.

MPEP§2163.07(a) states that disclosing a device that inherently performs a function or has a property, operates according to a theory or has an advantage necessarily discloses that function, theory or advantage, *even though it says nothing explicit concerning it."* (Emphasis supplied..) *"The application may later be amended to recite the function, theory, or advantage without introducing prohibited new mater."* In re Reynolds, 443 F.2d 384, 170 USPQ 94 (CCPA 1971); *In re Smythe,* 480 F.2d 1376, 178 USPQ 279 (CCPA 1973).

5.   The Examiner has failed to rebut Applicants' evidence that, at the time the applications were filed, one of ordinary skill in the art would recognize, in the specification disclosure of the Provisional and Subject Applications, a description of the invention defined by the claims.

"The examiner has the initial burden of presenting evidence or reasoning to explain why persons skilled in the art would not recognize in the original disclosure a description of the invention defined by the claims." MPEP§2163(I)(B)(3)(b). "The examiner, therefore, must have a reasonable basis to challenge the adequacy of the written description. The examiner has the initial burden of presenting by a preponderance of evidence why a person skilled in the art would not recognize in an applicant's disclosure a description of the invention defined by the claims." MPEP§2163.04. Further, "[u]pon reply by applicant, . . . [the examiner is required to] fully respond to applicant's rebuttal arguments, and properly treat any further showings submitted by applicant in the reply. When a rejection is maintained, any affidavits relevant to the 35 U.S.C. 112, para. 1, written description requirement, must be thoroughly analyzed and discussed in the next Office action." MPEP§2163.02.

The Niessen reference, cited by the Examiner to support his finding that the Subject and Provisional Applications fail to provide support for ash fluid temperature, actually supports the equivalence of ash fluid temperature and ash melting point or temperature.

At page 2 of the Office Action dated August 15, 2008, the Examiner attempts to rebut Applicants' evidence that a person skilled in the art would recognize in the applicant's disclosure a description of the invention defined by the claims. The Examiner has failed to respond as required by Section 112 to the Applicant's arguments in the Applicant's response dated March 24, 2008.

By way of example, the Examiner states simply:

As evidenced by Niessen the fluid temperature and melting point are two different physical properties. Consequently, since the specification is silent as to the term "fluid temperature" the specification would not have reasonably conveyed to one of ordinary skill that the application was in possession of the subject matter at the time of filing.

Nowhere is Niessen cited. Applicants assume that the single page entitled "Stoichiometry" attached to the Office Action is an excerpt from Niessen. For the convenience of the Examiner, this page is attached hereto as Exhibit "3". Because Applicant does not have a cite to Niessen, Applicant is unable to examine the context of discussion from which the page is taken. It appears that the reference is made in the context of an incinerator and not a coal furnace.

As can be seen from Exhibit "3", this page defines "Fluid Temperature" as "where the *molten* ash viscosity is very low and the material flows down the plate with a thickness *not greater* than 1/16th (0.15 cm). (Emphasis supplied.) This is the "flat" fluid temperature. (Exhibit "5"). "Molten" is defined as "melted or liquefied by heat". *Webster's New World Dictionary* (2nd Ed.). The thickness of the molten ash, or slag, is required to be *not more than* 1/16th inch or 0.15 cm. This thickness describes fully melted ash and ash at its "melting point". As noted by the Bisque Declaration (Exhibit "1"), the melting temperature or point of ash is the temperature at which "each of the lower melting point constituents have melted." (Bisque Declaration at ¶16.) *The attached page thus indicates that one of ordinary skill in the art would construe the term "melting temperature" or "melting point" (used in the Specification) in the context of ash to be the same as ash fluid temperature.*

> Benner, another reference cited by the Examiner, defines ash "melting temperature" or "melting point" to be the same as ash "fluid temperature".

In addition to the previously discussed articles and Bisque Declaration, Benner, a reference cited by the Examiner, is instructive on how one of ordinary skill in the art could construe the term "melting point" of ash. According to Benner, the "melting point" of the ash is:

the temperature at which it will prevent accumulation of slag on the furnace walls beyond a skin or coating which has been formed over the walls (which coating is produced by the air and/or water cooling of the furnace walls) and the congealing or setting of the slag in immediate contact therewith.

(page 2, lines 68-76.) This definition mirrors the fluid temperature definition of the page attached by the Examiner; therefore, one of ordinary skill in the art would understand, as

synonymous, the melting point or temperature of the ash on the one hand with fluid temperature on the other.

The above quoted passages and paragraphs 14 and 16 of the attached Bisque Declaration abundantly establish that one of ordinary skill in the art would understand the terms "melting temperature" or "melting point" of the ash on the one hand and "fluid temperature" of the ash on the other hand to be synonymous.

<u>The Examiner has dismissed the Bisque Declaration on improper grounds.</u>

In the Office Action mailed May 1, 2006, the Examiner states:

Paragraphs 14 and 15 of the Bisque declaration does [*sic*] not appear to support the conclusion that the terms melting point and ash fusion temperature are synonymous. Per the Bisque declaration the fluid temperature (FT) is defined as the temperature at which the ash cone *has melted* to a nearly flat layer with a maximum height of 0.0625 inches and requiring visual observation. This term does not appear to be synonymous with the term melting temperature. Consequently one of ordinary skill would not reasonably conclude that the inventor had possession of the claimed invention.

(Emphasis supplied)

In the final Office Action mailed December 6, 2006, the Examiner further states that "the affidavits were not prepared by disinterested third parties but by interested parties." (Final Office Action at p. 2.)

These paragraphs fail to provide supporting facts in at least two respects.

First, why does it "appear" that the terms melting point and fluid temperature are not synonymous. Apart from the fact that the declarant has stated under oath that this is the case, the Examiner fails to explain his position. The Examiner's own definition of fluid temperature references "melting" and requires the thickness of the melted ash to be no more than a specified thickness (which maximum thickness is synonymous with a melted ash layer). The definition further requires the ash cone (which has a standard size) to be liquefied. "Melt is defined by *Webster's New World Dictionary* as "to change from a solid to a liquid state, generally by heat". According to the Examiner's own definition, the fluid temperature is the temperature at which the last of the ash constituents has melted, or the ash melting temperature.

Second, the Examiner concludes, without support, that "one of ordinary skill would not reasonably conclude that the inventor had possession of the claimed invention." This conclusion is not only contrary to the conclusions in the Bisque Declaration but also does not follow from the prior sentences. As noted, the Bisque declaration and the Provisional and Subject Applications make clear that the iron-containing additive acts as a fluxing agent,

reduces the T_{250} temperature, reduces viscosity, and reduces the ash melting temperature. Even if fluid temperature is not synonymous with ash melting temperature, it still does not follow that the Provisional and Subject Applications do not convey to one of ordinary skill in the art at the time they were filed that the inventor had possession of the claimed invention.

Finally, the dismissal of affidavit evidence simply because it is not from a disinterested party is not a sufficient basis for failing to consider the affidavit. MPEP§716.01(a) states that affidavits or declarations, when timely presented, *must* be considered by the examiner in determining issues of patentability, particularly under 35 U.S.C.§103. MPEP§2163.07(a) states that extrinsic evidence is used to establish inherency and does not require that the extrinsic used to establish compliance of an amendment with the written description requirement be from a disinterested third party.

Accordingly, claims 24-26, 33-34, 36, 44-66, 73, 78-81, 87-88, 95, 100-102, 109-110, 122-124, 131-132, and 140-141comply with 35 U.S.C.§112, first paragraph.

Whether Claims 24-26, 33-34, 36, 44-53, 55-56, 61-66, 68-74, 76-77, 82-88, 90-96, 98-99, 104-110, 112-118, 120-121, 126-132, 134-137,and 139-141 are patentable under 35 U.S.C.§103(a) based on U.S. 1,955,574 to Benner in view of U.S. 4,572,085 to Hepworth.

35 U.S.C.§103(a) states that a patent may not be obtained . . . if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains.

The key to supporting any rejection under 35 U.S.C.§103 is the clear articulation of the reason(s) why the claimed invention would have been obvious. The Supreme Court in *KSR International Co. v. Teleflex Inc.*, 550 U.S. ___, ___, 82 USPQ2d 1385, 1396 (2007) noted that the analysis supporting a rejection under 35 U.S.C.§103 should be made explicit. The Federal Circuit has stated that "rejections on obviousness cannot be sustained with mere conclusory statements; instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness." *In re Kahn*, 441 F.3d 977, 988, 78 USPQ2d 1329, 1336 (Fed. Cir. 2006). *See also KSR*, 550 U.S. at ___ , 82 USPQ2d at 1396 (quoting Federal Circuit statement with approval).

If the examiner determines there is factual support for rejecting the claimed invention under 35 U.S.C.§103, the examiner must then consider any evidence supporting the patentability of the claimed invention, such as any evidence in the specification or any other

evidence submitted by the applicant. The ultimate determination of patentability is based on the entire record, by a preponderance of evidence, with due consideration to the persuasiveness of any arguments and any secondary evidence. *In re Oetiker*, 977 F.2d 1443, 24 USPQ2d 1443 (Fed. Cir. 1992). The legal standard of "a preponderance of evidence" requires the evidence to be more convincing than the evidence which is offered in opposition to it. With regard to rejections under 35 U.S.C.§103, the examiner must provide evidence which as a whole shows that the legal determination sought to be proved (i.e., the reference teachings establish a prima facie case of obviousness) is more probable than not.

1.   Benner teaches away from adding an iron-containing material to the coal boiler or furnace (Claims 24, 68, 90, 112, and 134).

Benner is directed to additives to raise or lower the melting point of ash to produce, during furnace operation, a thin layer of solid or very viscous slag on the furnace wall. This is realized when the flame temperature is between 50 to 350°C above the softening point of the ash as determined by pyrometric cones. The additives are rouge and fluxing or fusible clay to increase the melting point of the ash. (page 3, lines 23-51.) The clay additive is non-ferruginous (page 1, lines 71-75.) Ferruginous clays are clays that contain or have the nature of iron. *Webster's New World Dictionary* (2nd Ed.). Therefore, non-ferruginous clays do not contain or have the nature of iron. While acknowledging that the presence of iron can, depending on whether the atmosphere is oxidizing or reducing, be a chief cause of the melting point of the ash, Benner's use of non-ferruginous clay *teaches away* from adding iron to influence ash melting point. Iron-containing clays are disfavored because fire-clay bricks erode in the presence of iron (page 2, lines 103-112). The only additives Benner discloses are sand and non-ferruginous clays (to raise the softening point) and lime or soda (to lower the softening point).

2.   Hepworth teaches adding taconite and mill scale to control sulfur oxide emissions and says nothing about its impact on melting or fluid temperatures. (Claims 24, 68, 90, 112, and 134).

Hepworth is directed to a process for combusting sulfur-containing coal in a single step while producing an off-gas low in sulfur. The process comprises combusting finely divided coal in a furnace burner cavity in the presence of a finely divided iron oxide or iron powder and at least about 60% of the oxygen stoichiometrically required for substantially complete combustion of the coal to form a liquid iron oxysulfide phase and a turbulent atmosphere of combustion-product gases, liquid iron oxysulfide acting to scrub sulfur-

containing gaseous species from the atmosphere to yield an essentially sulfur-free flue gas and a liquid iron oxysulfide slag containing substantially the sulfur originally contained in the coal.

The process specifically discloses using fine high-sulfur coal and taconite or mill scale in a cyclone furnace to yield an essentially sulfur-free flue gas and a liquid iron oxysulfide slag containing essentially all of the sulfur in the feed coal. Hepworth states that "thermodynamic efficiency of the desulfurization process is improved since wustite serves as a diluent or solvent for FeS and reduces the H_2S pressure in equilibrium with the liquid, thereby contributing further to desulfurization of the gas." (Col. 5, lines 17-21.) Hepworth is silent about the effect of the iron oxide additive in lowering the melting point of the ash or in increasing slag viscosity.

3.   Hepworth teaches away from using taconite or mill scale to control melting point and rather teaches that carbon is effective in lowering the melting point (Claims 24, 68, 90, 112, and 134).

Hepworth further states that:

With the thermodynamic information available, it became possible to calculate gas compositions at the temperatures of interest. *In the calculation, the effect of carbon on the liquid phase was neglected.* The interaction coefficient is positive, indicating that carbon tends to raise the activity of sulfur. *A beneficial effect of carbon would be to lower the melting point of the liquid and hence increase its fluidity at a given temperature. The beneficial role of silica and other components in reducing the activity of the liquid was also neglected.*

(Emphasis supplied.)

Hepworth teaches away from using taconite or mill scale to control melting temperature by stating the carbon, not iron oxide, lowers the melting point of the liquid. Hepworth specifically neglected the beneficial role of "silica and other components in reducing the activity of the liquid".

4.   Hepworth is directed to high-sulfur eastern coals which can be metallurgically different from low sulfur western coals (or those having a sulfur content of less than about 1.5%) and therefore one of ordinary skill in the art could not predict, based on its teachings with a reasonable degree of success, the chemical results for low sulfur coals (Claims 24, 68, 90, 112, and 134).

Hepworth is directed to controlling sulfur dioxide emissions in *high*-sulfur eastern coals (col. 2, lines 26-27, col. 4, lines 25-32, col. 6, lines 23-24, col. 7, lines 18-22, col. 7,

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lines 45-49). Although fluxing by the iron additive may occur in the coal combustion process described by Hepworth for specific types of coals, it is far from being certain. Indeed, the only beneficial effect of iron oxide addition explicitly taught by Hepworth is a reduction in sulfur dioxide emissions. Whether iron acts as a flux depends not only on the valence state of the iron but also the composition of the coal. The constituents of coal ash are classed as either basic or acidic. Acidic consituents are silica, alumina, and titania while the basic constituents are iron, calcium, magnesium, and alkalies. As noted at col. 7, lines 21-28, and Fig. 3 of Shepard, a higher ratio of basic constituents indicates lower AFT characteristics or melting point of a fuel and therefore the basic constituents are considered to be the fluxes. For bituminous-type ash, the principle flux, or viscosity lowering, component is Fe_2O_3 while for lignite-type ash the principle fluxes are CaO and MgO. Switching to lower sulfur fuels will cause fuel ash with lower iron contents and lower basicity to be produced in the furnace, resulting in slag and handling problems due to higher than design ash viscosity characteristics. *Id.* at col. 7, lines 51-56.

> 5. Because of their divergent teachings, one of ordinary skill in the art would not combine Benner with Hepworth to produce the claimed invention. (Claims 24, 68, 90, 112, and 134).

Benner teaches away from ferruginous, or iron-containing, additives to influence ash softening point. Hepworth teaches that carbon, and not iron, lowers the melting point of the liquid (col. 5, lines 22-29.) Accordingly, one would not consider, and be unable to predict success, based on this combination of references, in adding iron to lower the melting or fluid temperatures of the ash.

> 6. Claims 69, 93, 115 and 139 provide further distinctions over Benner and Hepworth.

Claims 69, 93, and 139 require the solid fuel to include a coal having a total iron content of less than about 10 wt.% (dry basis of the ash), and wherein the coal has a calcium content of at least about 15 wt.% (dry basis of the ash). Claim 115 requires the solid fuel to have a total iron content of less than about 10 wt.% (dry basis of the ash), and wherein the solid fuel has an alkali content of at least about 20 wt. % (dry basis of the ash)

Neither Benner nor Hepworth disclose a coal having this composition. Benner teaches an Illinois bituminous coal having an Fe_2O content of 7.7 wt.% and a Kentucky bituminous coal having an Fe_2O content of 4.2 wt.%. Neither coal has a calcium content of

about 15 wt.% or greater. Moreover, claims 69 requires the coal to be sub-bituminous. Hepworth does not teach either the iron or calcium/alkali contents in these ranges.

Whether Claims 57-58, 78-79, 100-101, and 122-123 are patentable under 35 U.S.C.§103(a) based on Benner in view of Hepworth and further in view of U.S. 4,886,521 to Khan.

> 1. Khan fails to overcome the deficiencies of Benner and Hepworth.

Khan says nothing about the impact of iron oxide addition on ash melting or fluid temperature.

Khan is directed to the production of a fuel from the pyrolysis or gasification of coal or oil shale and specifically to the production of a fuel from the pyrolysis or gasification of coal or oil shale in the presence of iron oxide in an inert gas atmosphere. Iron oxide is mixed with the coal or oil shale feed to prevent the mixture from swelling. (Col. 3, lines 24-31). Hardening of coal causes coke formation.

> 2. Khan fails to teach or suggest the features of Claims 57-58, 78-79, 100-101, and 122-123.

Claims 57, 78, 100, and 122 require the iron-containing material to include at least one carbon compound. Claims 58, 79, 101, and 123 are directed to the iron-containing additive including a hydrocarbon, oil, grease, and/or xanthan gum.

The Examiner admits that both Benner and Hepworth are silent on this feature.

In addition to the arguments presented above, Khan says nothing about including one or more of these components in the iron oxide additive. For this teaching, the Examiner cites col. 1, lines 65-72, and col. 2, lines 1-32 of Khan. This passage does not mention any of these components let alone teach using such a compound "for the purpose of promoting removal of the slag." (Office Action at page 5.) Khan teaches prevention of coal or oil shale swelling during pyrolysis; it says nothing about slag removal.

Whether Claims 59-60, 80-81, 102-103, and 124-125 are patentable under 35 U.S.C.§103(a) based on Benner in view of Hepworth and further in view of U.S. 3,896,746 to Pirsh.

> 1. Pirsh fails to overcome the deficiencies of Benner and Hepworth.

Claims 59-60, 80-81, 102-103, and 124-125 require the boiler to include a particle size reduction device, a burner, a fuel transport system, and a combustion chamber.

Pirsch is directed to a system using vapor generator heating gases as a medium for removing moisture from the fuel before it is fired. Pirsch says nothing about iron addition to coal.

Whether Claims 54, 75, 97, and 119 are patentable under 35 U.S.C.§103(a) based on Benner in view of Hepworth and further in view of U.S. 4,089,507 to Arai, et al.

1. Arai, et al., fail to overcome the deficiencies of Benner and Hepworth.

Claims 54, 75, 97, and 119 require the iron-containing material to be dust from blast furnace gas cleaning equipment.

Arai, et al., are directed to manufacturing reduced pellets from the dust discharged from an iron foundry or steel mill. Arai, et al., like Pirsch, say nothing about iron addition to coal.

Whether Claims 68-86, 89-108, 111-130, and 133-139 are patentable under 35 U.S.C.§103(a) based Hepworth in view of U.S. 4,498,402 to Kober, et al.

The Examiner next rejects claims 68-86, 90-108, 111-130, and 133-139 under 35 U.S.C. §103(a) as being unpatentable over Hepworth (U.S. 4,572,085) in view of Kober (U.S. 4,498,402).

1.   Kober, et al., fail to overcome the deficiencies of Hepworth.

Hepworth is deficient for reasons noted above.

Kober, et al., fail to overcome the deficiencies of Hepworth. Kober, et al., are directed to the addition of conditioners, such as strontium carbonate, a mixture of zircon with copper oxychloride and a mixture of alumina with aluminum fluoride, zircon, or zirconyl chloride to control slagging. While disclosing low sulfur (western) coals, Kober, et al., say nothing about adding iron to coal to control melting temperature or point or fluid temperature.

2.   There is no motivation to combine the teachings of Hepworth and Kober, et al.

No motivation to combine the teachings of Hepworth and Kober can be found in the prior art. To the contrary, both Hepworth and Kober teach away from the combining the references. Indeed, one of skill in the art would have no reasonable expectation of success in

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combining Hepworth and Kober. Thus, a *prima facie* case of obviousness has not been extablished.

Nor is it obvious to modify the Hepworth process to use the low sulfur coal disclosed in Kober. Hepworth states, at col. 1, lines 22-32, as follows:

> Unfortunately, most of the coal supplies in the Eastern and Midwestern United States are *high in sulfur, and substitution of lower-sulfur Western coals therefore is not only expensive because of transportation cost but can cause further distress in the already economically deprived coal-mining areas.*
>
> It is accordingly desirable that economic means be found whereby available *high-*sulfur coals could be utilized without further contributing to the atmospheric pollution problem.

(Emphasis supplied.)

According to Hepworth, the cyclone burner was developed in the 1940's particularly for the purpose of burning high sulfur Illinois coal which has a high ash content and a low ash-fusion temperature. (Hepworth at col. 1, lines 35-38.)

> At col. 2, lines 26-37, Hepworth further states:
>
> Fine *high-sulfur* coal and iron oxide are combusted in a burner cavity such as that of a cyclone furnace using at least about 60% of the oxygen stoichiometrically required for completely combusting said coal to form a liquid iron oxysulfide phase and a turbulent atmosphere of combustion-product gases, with the liquid iron oxysulfide acting to scrub sulfur-containing gaseous species from the furnace atmosphere to yield an essentially sulfur-free flue gas and a liquid iron oxysulfide slag containing essentially all the sulfur contained in the feed coal. Temperature conditions are maintained between about 1100.degree. C. and 1500.degree. C.

As can be seen from the foregoing, the invention of Hepworth is specifically directed to the combustion of high *not* low sulfur coals in cyclone boilers because lower sulfur Western coals are expensive and, if used, can cause further distress in the already economically deprived Eastern coal-mining areas. Hepworth thus *teaches away* from using, in a cyclone boiler, low sulfur coals along with the iron additive of Hepworth. Moreover, because Hepworth teaches only that the iron additive removes sulfur and says nothing about its impact on the melting point or viscosity of the slag Hepworth provides no incentive or motivation to use low-sulfur coals with the additive in a wet bottom boiler.

Furthermore, Applicant respectfully submits that one of skill in the art would not simply use the low-sulfur coal of Kober with the teaching of Hepworth to meet environmental requirements. As discussed above, this replacement would frustrate the purpose of Hepworth, which is directed to reducing sulfur emissions by forming a liquid iron oxysulfide slag.

Moreover, one of skill in the art would have no reasonable expectation of success in combining the teachings of Hepworth and Kober due to the distinct chemical properties of high and low sulfur coals. It is well known to the skilled artisan that high and low sulfur coals differ not only in sulfur content, but also in ash content, iron content, and levels of magnesium and calcium. These chemical differences make some coals unsuitable for use in certain burners. For example, it is known in the art that the ash content of a coal and the total amount of sulfur compared to the ratio of iron to calcium and magnesium determines whether a coal is suitable for use in a cyclone furnace. Coals with a high iron ratio are unsuitable for use in these furnaces.

Kober also discloses that low-sulfur and high-sulfur coals are not interchangeable in boilers due to the vastly different chemical characteristics. Specifically, Kober states at col. 2, lines 6-15 in reference to switching from high- to low-sulfur coal sources:

> In many cases, these alternate coal supplies are *completely different* from the design coal with regard to ash fusion temperature, ash composition, etc. Substitution of coal with ash characteristics significantly different from those for which a boiler was designed can give rise to problems such as slagging.

(Emphasis supplied.)

The disclosure of Kober reinforces that known in the art: different coals are not interchangeable due to distinct chemistries. Kober thus teaches away from the combination of Hepworth and Kober, because one of skill in the art would not expect the combination to be successful.

3.   Claims 79, 101, and 123 are patentable over Hepworth and Kober, et al.

Claims 58, 79, 101, and 123 are directed to the iron-containing additive including a hydrocarbon, oil, grease, and/or xanthan gum.

Neither Hepworth nor Kober, et al., teach or suggest this feature.

4.   Claims 69, 93, 115 and 139 are patentable over Hepworth and Kober, et al.

Claims 69, 93, and 139 require the solid fuel to include a coal having a total iron content of less than about 10 wt.% (dry basis of the ash), and wherein the coal has a calcium content of at least about 15 wt.% (dry basis of the ash). Claim 115 requires the solid fuel to have a total iron content of less than about 10 wt.% (dry basis of the ash), and wherein the solid fuel has an alkali content of at least about 20 wt. % (dry basis of the ash)

Neither Kober, et al., nor Hepworth disclose a coal having this composition.

Accordingly, a prima *facie case* of obviousness has not been established. Applicant thus requests that these rejections be withdrawn.

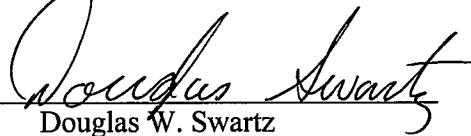The Board is thus respectfully requested to overturn the rejection.

Since the cited references fail to teach or suggest every claimed feature, whether taken alone or in combination, anticipation has not been established - the Board is respectfully requested to overturn the above rejections.

Remand to the Examiner with an indication of allowable subject matter is respectfully requested.

The Commissioner is hereby authorized to charge to deposit account number 19-1970 any fees under 37 CFR § 1.16 and 1.17 that may be required by this paper and to credit any overpayment to that Account. If any extension of time is required in connection with the filing of this paper and has not been separately requested, such extension is hereby petitioned.

Respectfully submitted,

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1-23. (Canceled)

24. A method of operating a solid fuel fired boiler, comprising:

introducing a solid fuel into the boiler, wherein the solid fuel is a coal having a sulfur content of less than about 1.5 wt.% (dry basis of the coal);

introducing an ironcontaining material into the boiler, wherein the iron-containing material is at least one of mill scale from steel production and dust from blast furnace gas cleaning equipment; and

at least partially combusting the solid fuel to produce an ash slag, wherein, in the at least partially combusting step, at least one of the following is true:

(i) the ash slag has a fluid temperature less than a fluid temperature characteristic of the ash slag produced from combustion of the solid fuel alone; and

(ii) the ash slag has a melting point less than the melting point of a second ash slag produced from the combustion of the solid fuel alone.

25. The method of claim 24, wherein the ash slag has a viscosity during the at least partially combusting step that is less than the viscosity of the second ash slag produced from combustion of the solid fuel alone.

26. The method of claim 24, wherein the ash slag has a melting point during the at least partially combusting step that is less than the melting point of the second ash slag produced from combustion of the solid fuel alone.

27-32. (Canceled)

33. The method of claim 24, wherein at least a portion of the iron-containing material fluxes the ash slag to produce a second ash slag having at least one characteristic selected from the group consisting of viscosity and melting temperature less than the same characteristic of the second ash slag produced from combustion of the solid fuel alone.

34. The method of claim 25, wherein a T_{250} temperature at which the ash slag has a viscosity of 250 poise produced from the combustion of the solid fuel and iron-containing material is at least 100 degrees Fahrenheit lower than the T_{250} temperature of the second ash slag produced from the combustion of the solid fuel alone.

35. (Canceled)

36. The method of claim 24, wherein the melting point of the second ash slag is less than 2600 degrees F.

37-43. (Canceled)

44. The method of claim 24, wherein (i) is true.

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45. The method of claim 24, wherein the fluid temperature is less than 2600 degrees F.

46. The method of claim 24, wherein (ii) is true.

47. The method of claim 24, wherein the solid fuel is introduced into a wet-bottom boiler.

48. The method of claim 24, wherein the solid fuel comprises a sub-bituminous coal and wherein the solid fuel has a low iron content and a high alkali content.

49. The method of claim 24, wherein the boiler is for at least one of steam production and electricity generation and wherein the iron-containing material has a P_{90} size of no more than about 300 microns.

50. The method of claim 24, wherein the boiler is a cyclone boiler.

51. The method of claim 24, wherein the ash slag has a viscosity such that the ash slag flows from the boiler.

52. The method of claim 50, further comprising reducing the particle size of the solid fuel prior to introducing the solid fuel into the boiler.

53. The method of claim 24, wherein the iron-containing material is mill scale from steel production.

54. The method of claim 24, wherein the iron-containing material is dust from blast furnace gas cleaning equipment.

55. The method of claim 24, wherein the iron-containing material comprises at least one of ferrous oxide and ferric iron oxide.

56. The method of claim 24, wherein the iron-containing material comprises magnetite.

57. The method of claim 24, wherein the iron-containing material comprises at least one carbon compound.

58. The method of claim 24, further comprising introducing at least one carbon compound along with the iron-containing material, the at least one carbon compound being one or more of a hydrocarbon, oil, grease, and xanthan gum.

59. The method of claim 24, wherein the boiler comprises:

a particle size reduction device, wherein the solid fuel is fed to the device;

a burner;

a fuel transfer system communicating with the device and the burner; and

a combustion chamber comprising an enclosure at least partially surrounding the burner and further comprising:

introducing the iron-containing material into at least one of the fuel storage bunker, the fuel transfer system, the cyclone burner, and the combustion chamber.

60.   The method of claim 50, wherein the cyclone boiler comprises:

a fuel storage bunker;

a cyclone burner;

a fuel transfer system communicating with the fuel storage bunker and the cyclone burner; and

a combustion chamber comprising an enclosure at least partially surrounding the burners.

61.   The method of claim 24, wherein the iron-containing material is introduced into the boiler in an amount ranging from about 10 lb/ton of solid fuel to about 50 lb/ton of solid fuel.

62.   The method of claim 24, wherein the ash slag has a total iron concentration of at least about 15 weight percent.

63.   The method of claim 50, wherein the iron-containing material is added to the solid fuel before introducing the solid fuel and the iron-containing material into the boiler.

64.   The method of claim 50, wherein the ash slag has a viscosity in the boiler less than the viscosity in the boiler of a second ash slag produced from the combustion of the solid fuel alone.

65.   The method of claim 24, wherein the iron-containing material is selected from the group consisting of ferrous oxide, ferric oxide, ferrous sulfide, ferric sulfide, and combinations thereof.

66.   The method of claim 44, wherein both (i) and (ii) are true.

67.   (Canceled)

68.   A method of operating a solid fuel fired boiler, comprising:

introducing a solid fuel into a wet-bottom boiler, wherein the solid fuel is a low sulfur coal having a sulfur content of less than about 1.5 wt.% (dry basis of the coal);

introducing an iron-containing material into the wet-bottom boiler, wherein the iron-containing material is at least one of mill scale from steel production and dust from blast furnace gas cleaning equipment; and

at least partially combusting the solid fuel to produce an ash slag, wherein at least a portion of the iron-containing material fluxes the ash slag to cause the ash slag to have a melting temperature less than the melting temperature of a second ash slag produced from the combustion of the solid fuel alone.

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69. The method of claim 68, wherein the solid fuel comprises a sub-bituminous coal, wherein the coal has a total iron content of less than about 10 wt.% (dry basis of the ash), and wherein the coal has a calcium content of at least about 15 wt.% (dry basis of the ash).

70. The method of claim 68, wherein the boiler is for at least one of steam production and electricity generation and wherein the iron-containing material has a P_{90} size of no more than about 300 microns.

71. The method of claim 68, wherein the boiler is a cyclone boiler.

72. The method of claim 68, wherein the ash slag has a viscosity such that the ash slag flows from the wet-bottom boiler.

73. The method of claim 68, further comprising reducing the particle size of the solid fuel prior to introducing the solid fuel into the boiler.

74. The method of claim 68, wherein the iron-containing material is mill scale from steel production.

75. The method of claim 68, wherein the iron-containing material is dust from blast furnace gas cleaning equipment.

76. The method of claim 68, wherein the iron-containing material comprises at least one of ferrous oxide and ferric iron oxide.

77. The method of claim 68, wherein the iron-containing material comprises magnetite.

78. The method of claim 68, wherein the iron-containing material comprises at least one carbon compound.

79. The method of claim 68, further comprising introducing at least one carbon compound along with the iron-containing material, the at least one carbon compound being one or more of a hydrocarbon, oil, grease, and xanthan gum.

80. The method of claim 68, wherein the wet-bottom boiler comprises:

a particle size reduction device, wherein the solid fuel is fed to the device;

a burner;

a fuel transfer system communicating with the device and the burner; and

a combustion chamber comprising an enclosure at least partially surrounding the burner and further comprising:

introducing the iron-containing material into at least one of the fuel storage bunker, the fuel transfer system, the cyclone burner, and the combustion chamber.

81. The method of claim 71, wherein the cyclone boiler

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comprises:

a fuel storage bunker;

a cyclone burner;

a fuel transfer system communicating with the fuel storage bunker and the cyclone burner; and

a combustion chamber comprising an enclosure at least partially surrounding the burners.

82. The method of claim 68, wherein the iron-containing material is introduced into the boiler in an amount ranging from about 10 lb/ton of solid fuel to about 20 lb/ton of solid fuel.

83. The method of claim 68, wherein the ash slag has a total iron concentration of at least about 15 weight percent.

84. The method of claim 68, wherein the iron-containing material is added to the solid fuel before introducing the solid fuel and the iron-containing material into the boiler.

85. The method of claim 68, wherein the second ash slag has a viscosity in the boiler less than the viscosity in the boiler of the ash slag produced from the combustion of the solid fuel alone.

86. The method of claim 68, wherein the iron-containing material is selected from the group consisting of ferrous oxide, ferric oxide, ferrous sulfide, ferric sulfide, and combinations thereof.

87. The method of claim 68, wherein, in the at least partially combusting step, a fluid temperature of the ash slag is less than the a fluid temperature of a second ash slag produced from combustion of the solid fuel alone.

88. The method of claim 87, wherein the fluid temperature is less than 2600°F.

89. (Canceled)

90. A method of operating a solid fuel fired boiler, comprising:

introducing a solid fuel into a wet-bottom boiler, the solid fuel comprising a low sulfur coal having a sulfur content of less than about 1.5 wt.% (dry basis of the coal);

introducing an iron-containing material into the wet-bottom boiler, wherein the iron-containing material is at least one of mill scale from steel production and dust from blast furnace gas cleaning equipment; and

at least partially combusting the solid fuel to produce an ash slag, wherein at least a portion of the iron-containing material fluxes the ash slag to cause the ash slag to have a

viscosity in the boiler less than the viscosity in the boiler of a second ash slag produced from the combustion of the solid fuel alone.

91. The method of claim 90, wherein the solid fuel comprises a sub-bituminous coal.

92. The method of claim 90, wherein the boiler is for at least one of steam production and electricity generation and wherein the iron-containing material has a P_{90} size of no more than about 300 microns.

93. The method of claim 90, wherein the boiler is a cyclone boiler, wherein the low sulfur coal has a total iron content of less than about 10 wt.% (dry basis of the ash), and wherein the low sulfur coal has a calcium content of at least about 15 wt.% (dry basis of the ash).

94. The method of claim 90, wherein the ash slag has a viscosity such that the ash slag flows from the wet-bottom boiler.

95. The method of claim 90, further comprising reducing the particle size of the solid fuel prior to introducing the solid fuel into the boiler.

96. The method of claim 90, wherein the iron-containing material is mill scale from steel production.

97. The method of claim 90, wherein the iron-containing material is dust from blast furnace gas cleaning equipment.

98. The method of claim 90, wherein the iron-containing material comprises at least one of ferrous oxide and ferric iron oxide.

99. The method of claim 90, wherein the iron-containing material comprises magnetite.

100. The method of claim 90, wherein the iron-containing material comprises at least one carbon compound.

101. The method of claim 90, further comprising introducing at least one carbon compound along with the iron-containing material, the at least one carbon compound being one or more of a hydrocarbon, oil, grease, and xanthan gum.

102. The method of claim 90, wherein the wet-bottom boiler comprises:

a particle size reduction device, wherein the solid fuel is fed to the device;

a burner;

a fuel transfer system communicating with the device and the burner; and

a combustion chamber comprising an enclosure at least partially surrounding the burner and further comprising:

introducing the iron-containing material into at least one of the fuel storage bunker, the fuel transfer system, the cyclone burner, and the combustion chamber.

103.   The method of claim 93, wherein the cyclone boiler comprises:

a fuel storage bunker;

a cyclone burner;

a fuel transfer system communicating with the fuel storage bunker and the cyclone burner; and

a combustion chamber comprising an enclosure at least partially surrounding the burners.

104.   The method of claim 90, wherein the iron-containing material is introduced into the boiler in an amount ranging from about 10 lb/ton of solid fuel to about 50 lb/ton of solid fuel.

105.   The method of claim 90, wherein the ash slag has a total iron concentration of at least about 15 weight percent.

106.   The method of claim 90, wherein the iron-containing material is added to the solid fuel before introducing the solid fuel and the iron-containing material into the boiler.

107.   The method of claim 90, wherein the ash slag has a melting temperature less than the melting temperature of the second ash slag produced from the combustion of the solid fuel alone.

108.   The method of claim 90, wherein the iron-containing material is selected from the group consisting of ferrous oxide, ferric oxide, ferrous sulfide, ferric sulfide, and combinations thereof.

109.   The method of claim 90, wherein, in the at least partially combusting step, a fluid temperature of the ash slag is less than a fluid temperature of the second ash slag produced from combustion of the solid fuel alone.

110.   The method of claim 109, wherein the fluid temperature is less than 2600°F.

111.   (Canceled)

112.   A method of operating a solid fuel fired boiler, comprising:

introducing a solid fuel into a wet-bottom boiler, the solid fuel comprising a low sulfur coal having a sulfur content of less than about 1.5 wt.% (dry basis of the coal);

introducing an iron-containing material into the wet-bottom boiler, wherein the iron-containing material comprises iron oxides; and

at least partially combusting the solid fuel to produce an ash slag, wherein at least a portion of the iron-containing material fluxes the ash slag to cause the ash slag to have a

viscosity less than a viscosity of a second ash slag produced from the combustion of the solid fuel alone.

113. The method of claim 112, wherein the solid fuel comprises a sub-bituminous coal.

114. The method of claim 112, wherein the boiler is for at least one of steam production and electricity generation and wherein the iron-containing material has a P_{90} size of no more than about 300 microns.

115. The method of claim 112, wherein the boiler is a cyclone boiler, wherein the solid fuel has a total iron content of less than about 10 wt.% (dry basis of the ash), and wherein the solid fuel has an alkali content of at least about 20 wt. % (dry basis of the ash).

116. The method of claim 112, wherein the ash slag has a viscosity such that the ash slag flows from the wet-bottom boiler.

117. The method of claim 112, further comprising reducing the particle size of the solid fuel prior to introducing the solid fuel into the boiler.

118. The method of claim 112, wherein the iron-containing material is mill scale from steel production.

119. The method of claim 112, wherein the iron-containing material is dust from blast furnace gas cleaning equipment.

120. The method of claim 112, wherein the iron-containing material comprises at least one of ferrous oxide and ferric iron oxide.

121. The method of claim 112, wherein the iron-containing material comprises magnetite.

122. The method of claim 112, wherein the iron-containing material comprises at least one carbon compound.

123. The method of claim 112, further comprising introducing at least one carbon compound along with the iron-containing material, the at least one carbon compound being one or more of a hydrocarbon, oil, grease, and xanthan gum.

124. The method of claim 112, wherein the wet-bottom boiler comprises:

a particle size reduction device, wherein the solid fuel is fed to the device;

a burner;

a fuel transfer system communicating with the device and the burner; and

a combustion chamber comprising an enclosure at least partially surrounding the burner and further comprising:

introducing the iron-containing material into at least one of the fuel storage bunker, the fuel transfer system, the cyclone burner, and the combustion chamber.

125.   The method of claim 115, wherein the cyclone boiler comprises:

a fuel storage bunker;

a cyclone burner;

a fuel transfer system communicating with the fuel storage bunker and the cyclone burner; and

a combustion chamber comprising an enclosure at least partially surrounding the burners.

126.   The method of claim 112, wherein the iron-containing material is introduced into the boiler in an amount ranging from about 10 lb/ton of solid fuel to about 20 lb/ton of solid fuel.

127.   The method of claim 112, wherein the ash slag has a total iron concentration of at least about 15 weight percent.

128.   The method of claim 112, wherein the iron-containing material is added to the solid fuel before introducing the solid fuel and the iron-containing material into the boiler.

129.   The method of claim 112, wherein the ash slag has a melting point in the boiler less than the melting point in the boiler of the second ash slag produced from the combustion of the solid fuel alone.

130.   The method of claim 112, wherein the iron-containing material is selected from the group consisting of ferrous oxide, ferric oxide, ferrous sulfide, ferric sulfide, and combinations thereof.

131.   The method of claim 112, wherein, in the at least partially combusting step, a fluid temperature of the ash slag is less than the a fluid temperature of the second ash slag produced from combustion of the solid fuel alone.

132.   The method of claim 131, wherein the the fluid temperature is less than 2600°F.

133.   (Canceled)

134.   A method for operating a slag type furnace, comprising:

introducing a coal-containing fuel into said slag type furnace, the coal-containing fuel comprising a low sulfur coal having a sulfur content of less than about 1.5 wt.% (dry basis of the coal);

introducing an iron-containing additive into the slag type furnace in an amount sufficient to flux the coal-containing fuel; and

melting at least a portion of the coal-containing fuel to produce an ash slag, wherein, in the melting step, at least a portion of the iron-containing additive fluxes the ash slag to produce a slag layer having a melting point less than a melting point of a second slag layer without the iron-containing additive.

135.   The method of claim 134, wherein at least about 33.5% of the iron-containing additive is in the form of ferrous iron and no more than about 66.5% of the iron in the additive is in the form of ferric iron.

136.   The method of claim 134, wherein the additive is in the form of a free-flowing particulate having a P_{90} size of no more than about 300 microns.

137.   The method of claim 1, wherein the additive comprises one or more of mill scale fines and particles removed by particulate collection systems from one or more of offgases of steel manufacturing and offgases from iron manufacturing, and wherein the coal-containing fuel has a total iron content of less than about 10 wt.% (dry basis of the ash).

138.   (Canceled)

139.   The method of claim 134, wherein the coal-containing fuel has a total iron content of less than about 10 wt. % (dry basis of the ash) and a calcium content of at least about 15 wt. % (dry basis of the ash).

140.   The method of claim 24, wherein the boiler is a slag-tap furnace.

141.   The method of claim 24, wherein the solid fuel boiler is used for at least one of steam production and electricity generation.

142.   (Canceled)

(ix) EVIDENCE APPENDIX.

The following documents are attached:

Exhibit "1"   Declaration of Ramon Bisque under 37 C.F.R.§(including attached
article *"Steam/its generation and use"*).

Exhibit "2"   Article *"Coal Properties, Sampling & Ash Characteristics"*

Exibit "3"   U.S. Patent 6,484,651 to Shepard, Jr., et al.

Exhibit "4"   Page attached to Office Action.

Exhibit "5"   Page8-9 attached to Babcock & Wilcox, *Steam its generation and use*

(x) RELATED PROCEEDINGS APPENDIX.

None.

EXHIBIT 1

<center>IN THE UNITED STATES PATENT AND TRADEMARK OFFICE</center>

In Re the Application of:)	Group Art Unit: 3749
)	
JOHNSON et al.)	Examiner: RINEHART, KENNETH
)	
Serial No.: 10/622,677)	DECLARATION OF RAMON BISQUE
)	UNDER 37 C.F.R. §1.132
Filed: July 18, 2003)	

Atty. File No.: 3791-13-CON   )

For: "LOW SULFUR COAL ADDITIVE   )
        FOR IMPROVED FURNACE   )
        OPERATION"   )

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313

Dear Sir:

I, Ramon Bisque, state as follows:

1.   I received a Bachelor of Science in Chemistry from St. Norbert College in 1953; a Master of Science in Chemistry from Iowa State University in 1956; a Master of Science in Geology from Iowa State University in 1957; and a Ph. D. in Geology-Chemistry from Iowa State University in 1959.

2.   I have been a certified professional geologic scientist since 1967 and am a Fellow of the American Association for the Advancement of Science.

3.   From 1959 through 1990, I was a professor at the Colorado School of Mines, for which employment I have been designated as a Professor Emeritus. During 1964 through 1967, I was on leave from the Colorado School of Mines and was initially an Associate Director/Consultant and later a Director of the Earth Science Curriculum Project for the American Geological Institute. I was a co-founder of Earth Sciences, Inc., (at one time the parent of both ADA Environmental Solutions, LLC and ADA Environmental Solutions, Inc.) and have

been employed by the company from 1972 to present. During my career, I have been involved in a wide diversity of areas including resource exploration and development, soil geochemistry, weathering, exploration geochemistry, analysis of mechanisms of silicate reactions, collection and determination of trace elements, and utility flue gas contaminant removal. Since 1997, I have been involved on behalf of ADA Environmental Solutions, Inc., in analyzing the results of full-scale testing of additives utilized in coal-fired power plants. These analyses were performed to understand the mechanisms of key reactions involved and attempt to move from the art to science" with the ultimate goal of predicting behavior of other additives.

4. In these areas, I have authored, solely or jointly with others, 27 published articles and two books.

5. I submit that I am qualified to testify as to the understanding of one of ordinary skill in the relevant arts of chemistry and geochemistry at the time the above-identified application and the provisional application (from which the above-identified application claims priority) were filed.

6. I am a shareholder (less than 5% of the outstanding stock), Chairman of the Board of Directors, and a part-time employee of ADA Environmental Solutions, Inc., which wholly owns ADA Environmental Solutions, LLC, the assignee of the above application. I am not an inventor of the above application.

7. In connection with the Office Action mailed January 29, 2004, I reviewed the following documents: (a) the Office Action; (b) U.S. Patent 6,484,651 to Shepard, Jr., et al. ("the Shepard Patent"); (c) the above application ("the Subject Application"); and (d) U.S. Provisional Application Serial No. 60/213,915, filed June 26, 2000, entitled "Low-Cost Technology to Improve Operation of Cyclone Furnaces Firing Low-Sulfur Western Coals" ("Provisional Application") from which the Subject Application claims priority.

8.   At the outset, it is important to understand that, in certain embodiments, the Provisional Application, Subject Application, and Shepard Patent are directed to the same invention. They each disclose the combustion of the same fuel in the same type of combustion chamber in the presence of the same iron-bearing material additive under the same temperature regime. The fuel is a low sulfur western or eastern coal (*see, e.g.,* Provisional Application at pages 1 and 3; Subject Application at Figure 2, page 2, lines 15-17, page 3, lines 9-12, page 4, lines 3-4 and 7-9, and page 6, lines 4-5; and Shepard Patent at col. 1, line 62-col. 2, line 3, col. 3, lines 26-34 and 55-57and Fuels 3 and 4). The combustion chamber is a "slag tap" or "wet bottom" boiler, such as a cyclone-type boiler (*see, e.g.,* Provisional Application at pages 1-5 and 7-8; Subject Application at Figure 1, page 1, lines 18-26, page 5, lines 16-17, page 6, lines 4-5 and 15-18, and page 18, lines 12-13; and Shepard Patent at col. 2, lines 7-8, col. 4, lines 7-10). The iron-bearing material is mill scale from steel production or dust from blast furnace gas cleaning equipment (*see, e.g.,* Provisional Application at pages 4 and 6; Subject Application at page 12, lines 7-12; and Shepard Patent at col. 4, lines 15-16, col. 8, lines 4-5). The temperature regime is that necessary to combust the solid fuel and melt the ash content of the fuel to form slag. (*see, e.g.,* Provisional Application at pages 1-5 and 7-8; Subject Application at page 2, lines 14-15, page 6, lines 4-5 and lines 15-18, Figures 7-8 and page 20, lines 1-21; and Shepard Patent at col. 2, lines 4-50, col. 5, lines 10-50). In chemistry, it is elementary that the use of the same reactants under the same reaction conditions in the same reactor will produce the same results. Thus, the various claim limitations discussed below are inherent in the disclosures of the Provisional and Subject Applications.

9.   At page 3 of the Office Action, the Examiner states that the carbon compound limitation of claim 1 of the Subject Application, namely that "at least one carbon compound promoting reduction of iron oxides" be introduced along with the iron-bearing material, fails to comply with the written description requirement of 35 U.S.C.§112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to

reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

10.   I disagree. Although the Shepard patent fails to identify the precise carbon compound(s) referenced by this phrase, it states at col. 8, lines 13-16, that "[c]arbon may be present in the iron-bearing materials in the form of, for example, blast furnace flue dust, or carbon may be added to these materials to promote reduction of the iron oxides to more readily flux the fuel ash." From this sentence, it is my understanding that the carbon referenced in the Shepard patent is in the form of elemental carbon, coke, and/or hydrocarbons. The Subject and Provisional Applications each reference a number of carbon compounds that would be understood by one of ordinary skill in the art to promote reduction of iron oxides, such as hematite, magnetite, and wustite, under the thermal conditions of the combustion chamber. These compounds include hydrocarbons in the coal feed itself (Provisional Application at page 7 and Subject Application at page 6, lines 6-14); oils and greases (Provisional Application at page 4 and Subject Application at page 12, lines 14-17); xanthum gum (Provisional Application at page 6 and Subject Application at page 13, lines 10-13); and residual hydrocarbons remaining in the boiler slag, which may be added to the iron-bearing material as a flow aid (Provisional Application at page 8 and Subject Application at page 15, lines 1-2). Moreover, as admitted in part by the Shepard patent, iron-oxide reducing carbon compound(s) will be inherently present in the iron-bearing material itself when the iron-bearing material is a byproduct of steel and iron manufacturing, such as Basic Oxygen Furnace or BOF flue dust or precipitator fines, blast furnace flue dust, electric arc furnace dust, and mill scale fines (Provisional Application at page 4 and Subject Application at page 12, lines 7-12, and page 18, lines 13-14).

11.   For these reasons, one of ordinary skill in the art, based on the Specifications of the Subject and Provisional Applications, would conclude that, at the time each application was filed, the inventors had possession of an iron-containing additive containing at least one carbon compound to promote reduction of iron oxides in the iron-containing additive.

12.   At pages 3 and 5 of the Office Action, the Examiner states that the Ash Fusion Temperature or AFT-characteristic limitation of claims 1, 19, and 24 of the Subject Application, namely that an ash slag produced by combusting the solid fuel in the presence of the iron-bearing material has "at least one ash fusion temperature characteristic selected from the group consisting of initial deformation temperature, softening temperature, hemispherical temperature, and fluid temperature is less than the same ash fusion temperature characteristic of a second ash slag produced from combustion of the solid fuel alone", fails to comply with the written description requirement of 35 U.S.C.§112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

13.   I disagree. The Subject and Provisional Applications each state that the iron-bearing additive fluxes the ash (Provisional Application at pages 3-4, 5, and 7 and Subject Application at page 5, lines 13-14, page 6, lines 19-22, page 8, lines 10-11) and lowers the melting temperature of the ash (Provisional Application at page 1 and Subject Application at page 7, lines 15-18, Figures 7-8, and page 20, lines 1-21). The AFT characteristics of initial deformation temperature, softening temperature, hemispherical temperature, and fluid temperature represent a continuum of constituent melting points leading to the complete melting of the ash. The characteristics are arbitrary and established by subjective visual observation.

14.   According to pages 20-5 through 20-7 of *"Steam/its generation and use"*, by Babcock & Wilcox (1972) ("the Babcock & Wilcox Article" attached hereto as Exhibit "A"), the AFT properties are determined as part of the ASTM Standard D 1857, *Fusibility of Coal and Coke Ash"*. According to the standard, an ash sample is prepared by burning coal under oxidizing conditions at temperatures of 1470 to 1650°F. The ash is pressed into a mold to form a triangular pyramid cone 0.75 in. in height with a 0.25 in. triangular base. The cone is heated in a furnace at a controlled rate to provide a temperature increase of 15°F per minute. The initial

deformation temperature (IT or ID) refers to the temperature at which the tip of the pyramid begins to fuse or show signs of deformation. The softening temperature (ST) is the temperature at which the sample has deformed to a spherical shape where the height of the cone is equal to the width at the base (H=W). The softening temperature is commonly referred to as the fusion temperature. The hemispherical temperature (HT) is the temperature at which the cone has fused down to a hemispherical lump and the height equals one half the width of the base (H=1/2W). The fluid temperature (FT) is the temperature at which the ash cone has melted to a nearly flat layer with a maximum height of 0.0625 in.

15.   It is well known that each of the AFT characteristics, namely IT, ST, HT, and FT, represent a melting point of one or more ash constituents. Regarding the relationship between the AFT properties and the melting point of the ash, the Babcock & Wilcox Article states:

> The gradual deformation of the ash cone is generally considered to result from differences in melting characteristics of the various ash constituents. As the temperature of the sample is increased, compounds with lowest melting temperature begin to melt, causing the initial deformation. As the temperature continues to increase, more of the compounds melt and the degree of deformation proceeds to the softening and hemispherical stages. The process continues until the temperature is higher than the melting point of most of the ash constituents and the fluid stage is reached.

(The Babcock & Wilcox Article at page 20-6.)

16.   For at least these reasons at the times that the Subject and Provisional Applications were filed, one of ordinary skill in the art would understand the phrase, "melting temperature of the ash" (as used in the Subject and Provisional Applications), to refer to the last (or highest) of a sequence of melting points for differing ash constituents and require that each of the lower melting point constituents have melted. The melting temperature of the ash is therefore synonymous with the fluid temperature.

17. Regarding the AFT-characteristic limitation and the fluxing limitation, namely that the "iron bearing material fluxes the ash slag" in claims 1, 11, 19, 24 and 33 (*see* Office Action at pages 3, 4, 5, and 33), the Provisional and Subject Applications further use the term "flux" and "fluxing agent". (Provisional Application at pages 1, 3-4, and 6-8 and Subject Application at page 5, lines 13-14, page 6, lines 19-22, page 8, lines 10-11). According to *Hawley's Condensed Chemical Dictionary*, "flux" is defined as "[a] substance that promotes fusing of minerals or metals or prevents the formation of oxides." It further defines "fuse" as "[o]f a solid, to *melt*, e.g., a fused salt." (Emphasis supplied.) The terms "flux" and "fuse" would further suggest to one of ordinary skill in the art that the various melting points of the ash constituents, denoted by the AFT properties, are lowered by the iron-bearing additive disclosed in the Provisional and Subject Applications.

18. The Provisional and Subject Applications further refer to the iron-containing additive lowering the T_{250} (or the temperature at which the ash would have a viscosity of 250 poise and is an important indicator for the minimum temperature at which the slag will flow) for low-sulfur eastern and western coals having low iron and high calcium contents. (Provisional Application at pages 1 and 4-5 and Subject Application at Figure 2, page 2, lines 15-17, page 7, lines 15-18, page 9, lines 14-15, page 19, lines 5-10, Figures 7-8 and page 20, lines 3-21). As shown in Figure 7 of the Subject Application, the iron-containing additive lowers the slag viscosity, at temperatures above about 2275°F, compared to a slag when no additive is used. It is inherent that the use of the iron-bearing material to lower the T_{250} of low-sulfur coals having low iron and high calcium contents will lower each of the AFT properties referenced above.

19. For at least the reasons set forth above, the AFT-characteristic and fluxing limitations are each described in the Specifications of both the Provisional and Subject Applications in such a way as to reasonably convey to one skilled in the relevant art that

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the inventors, at the time each of the applications was filed, had possession of the claimed invention.

20. Claims 1, 19, and 24 further require the iron-bearing material to cause a reduction in at least one AFT characteristic and ash slag melting point relative to the ash slag in the absence of the iron-bearing material. The Provisional and Subject Applications further refer to the iron-containing additive lowering the T_{250} (or the temperature at which the ash would have a viscosity of 250 poise and is an important indicator for the minimum temperature at which the slag will flow) for low-sulfur western and eastern coals having low iron and high calcium contents. (Provisional Application at pages 1 and 4-5 and Subject Application at Figure 2, page 2, lines 15-17, page 7, lines 15-18, page 9, lines 14-15, page 19, lines 5-10, Figures 7-8 and page 20, lines 3-21). As shown in Figures 7-8 of the Subject Application, the iron-containing additive lowers the slag viscosity, at temperatures above about 2275°F, compared to a slag when no additive is used. It is inherent that lowering the T_{250} of low-sulfur coals having low iron and high calcium contents will lower each of the AFT properties referenced above.

21. Finally, at pages 4, 5, and 6 of the Office Action, the Examiner states that the claimed requirements (of claims 3, 17, 22, and 36) that the at least one AFT characteristic or melting point of the composite ash slag be less than 2,600°F fail to comply with the written description requirement of 35 U.S.C.§112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

22. I disagree. The Provisional Application at page 1 and the Subject Application at page 2, lines 14-15, disclose that the ash (from which the molten slag is formed), in cyclone boilers, must be melted at normal combustion temperatures ranging

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from 2,600 to 3,000°F. Moreover, the Subject Application at page 20 and in Figure 7 shows that the ash/slag is melted at a temperature below 1,900°F.

23.   For at least the reasons set forth above, the requirement referenced in ¶21 is described in the Specifications of both the Provisional and Subject Applications in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time each of the applications was filed, had possession of the claimed invention.

24.   I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully submitted,

Date: _July 29, 2004_   By: _Ramon Bisque_

Steam /its generation and use

Babcock & Wilcox
161 East 42nd Street, New York, N.Y. 10017

Chapter 10

Cyclone Furnaces

Over the years continuing advances have been made in the methods of burning coal. The introduction of pulverized-coal firing in the 1920's was a major advance, providing advantages over stoker firing as listed in Chapter 9. Today, pulverized-coal firing is highly developed and is still the best way to burn many types of coal, particularly the higher grades and ranks.

However, during the last 35 years, another method of burning coal, the Cyclone Furnace, has been developed and is now widely used. Cyclone-Furnace firing represents the most significant advance in coal firing since the introduction of pulverized coal.

The Cyclone Furnace is applicable to coals having a slag viscosity of 250 poises at 2600F or lower, provided the ash analysis does not indicate excessive formation of iron or iron pyrites (see *Suitability of Fuels for the Cyclone Furnace*). With these coals, Cyclone-Furnace firing provides the benefits obtainable with pulverized-coal firing plus the following advantages:

1. Reduction in fly ash content in the flue gas.

2. Saving in the cost of fuel preparation, since only crushing is required instead of pulverization.

3. Reduction in furnace size.

For further understanding a discussion of the combustion of coal particles may be helpful, particularly if this is considered in the framework of the "three T's" of combustion (Chapter 6) with special emphasis on turbulence (mixing) and time.

When coal is burned in boiler furnaces, the combustion of hydrogen is accomplished without difficulty, but successful combustion of carbon to CO_2 requires special measures to assure a continuing supply of oxygen in contact with carbon particles as long as they remain unburned. Not only must there be intimate mixing of the coal particles and air; there must also be sufficient turbulence to remove the combustion products as they form at the surface of the fuel and provide fresh air at the fuel surface to continue combustion. The greater the turbulence the more rapid the process; hence less time is required for combustion.

With pulverized-coal firing, the coal is reduced to a powder, so fine that approximately 70 percent will pass a 200-mesh screen. The finely pulverized coal is then very intimately mixed with combustion air in the burner, however, after this initial mixing the tiny coal particles are merely carried along in the air stream, and very little additional scrubbing by the air occurs. Thus, further contact of oxygen with the coal must be largely by diffusion. The furnace consequently has to be relatively large to give the necessary retention time for oxygen to diffuse through the blanketing CO_2 layer to reach the coal particles and, at the same time, temperatures must be sufficiently high to complete combustion. After combustion, since the residual ash particles are much smaller than even the original tiny pulverized-coal particles, the former are easily carried along with the flue gases from the furnace and through the boiler setting.

At the same time the pulverized-coal-fired boiler furnace also has the function of cooling the combustion
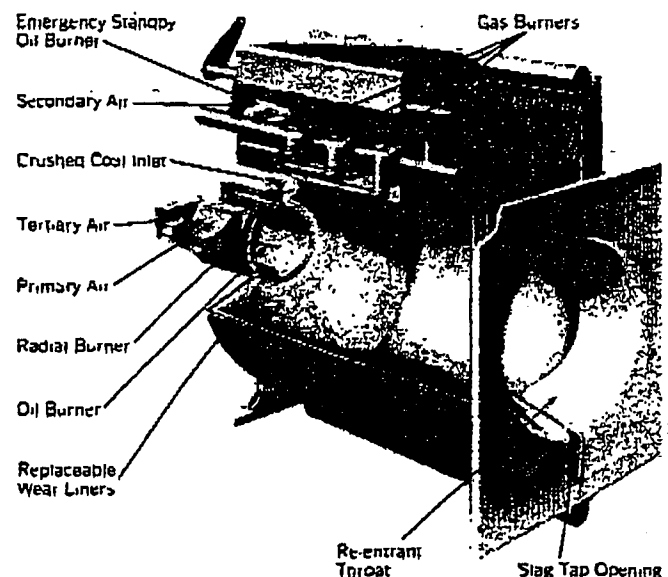

Fig. 1 The Cyclone Furnace, in the form of a horizontal cylinder, is completely water cooled by connection to the main boiler circulation. All combustion gases leave through the re-entrant throat at the rear. Molten slag drains from the bottom at the rear through a small opening into the adjacent boiler furnace.

gases, so that when they enter the convection surfaces they are below the temperature at which slagging occurs. This function conflicts with that of maintaining the high temperatures necessary to complete combustion. It would therefore be advantageous to separate these functions by providing a separate small combustion chamber where high turbulence and temperature may be maintained, and using the main boiler furnace primarily to cool the combustion gases.

For many years engineers recognized this need and actively explored basic changes in the design of furnaces and fuel-burning equipment to improve combustion and furnace performance. In addition, significant changes in availability and use of coal further increased the need for new designs, e.g., demands for higher grades of coal have depleted many seams, and others have been reserved for metallurgical and other uses. Mechanization in coal mining has increased the ash content of mined coal.

Washing is widely used to lower ash and sulfur contents; however, this is an added expense (see Chapter 8). The industrial growth of the Western portion of the country, rich in reserves of subbituminous and lignitic coal, is rapidly increasing the consumption of these lower ranks of coal. This has furthered the need for equipment fully suitable for the lower grades and ranks of high-ash, low-fusion-temperature coal. The Cyclone Furnace is an outgrowth of efforts to meet these needs and to overcome difficulties encountered with other firing methods.

Principle of operation

The Cyclone Furnace (Fig. 1) is a water-cooled horizontal cylinder in which fuel is fired, heat is released at extremely high rates, and combustion is completed. Its water-cooled surfaces are studded, and covered with refractory over most of their area (see Chapter 16). Coal crushed in a simple crusher, so that approximately 95 percent will pass a 4-mesh screen, is introduced into the burner end of the cyclone. About 20 percent of the combustion air, termed primary air, also enters the burner tangentially and imparts a whirling motion to the incoming coal. Secondary air with a velocity of approximately 300 fps is admitted in the same direction tangentially at the roof of the main barrel of the cyclone and
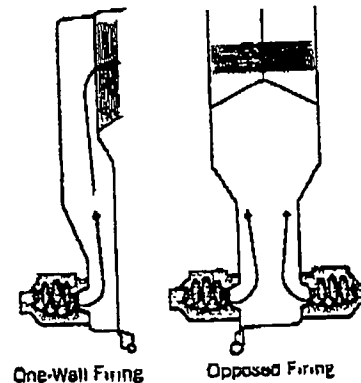

One-Wall Firing   Opposed Firing

Fig. 3 Firing arrangements used with Cyclone Furnaces.

imparts a further whirling or centrifugal action to the coal particles. A small amount of air (up to about 5%) is admitted at the center of the burner. This is known as "tertiary" air (Fig. 1).

The combustible is burned from the fuel at heat release rates of 450,000 to 800,000 Btu/cu ft, hr, and gas temperatures exceeding 3000F are developed. These temperatures are sufficiently high to melt the ash into a liquid slag, which forms a layer on the walls of the cyclone. The incoming coal particles (except for a few fines that are burned in suspension) are thrown to the walls by centrifugal force, held in the slag, and scrubbed by the high-velocity tangential secondary air. Thus the air required to burn the coal is quickly supplied, and the products of combustion are rapidly removed.

The release of heat per cu ft in the Cyclone Furnace is very high. However, there is only a small amount of surface in the cyclone and this surface is partially insulated by the covering slag layer. Heat absorption rates range from 40,000 to 80,000 Btu/sq ft, hr. This combination of high heat release and low heat absorption assures the high temperatures necessary to complete combustion and to provide the desired liquid slag covering of the surface.

The gaseous products of combustion are discharged through the water-cooled re-entrant throat of the cyclone (Fig. 1) into the gas-cooling boiler furnace. Molten slag in excess of the thin layer retained on the walls continually drains away from the burner end and discharges through the slag tap opening, shown in Fig. 1, to the boiler furnace, from which it is tapped into a slag tank, solidified, and disintegrated for disposal (see Slag Handling Equipment).

By this method of combustion the fuel is burned quickly and completely in the small cyclone chamber, and the boiler furnace is used only for cooling the flue gases. Most of the ash is retained as a liquid slag and tapped into the slag tank under the boiler furnace. Thus, the quantity of fly-ash is low and its particle size so fine that erosion of boiler heating surfaces is not experienced even at high gas velocities.

Suitability of fuels for the Cyclone Furnace

The Cyclone Furnace is capable of burning successfully a large variety of fuels. A wide range of coals varying in rank from low volatile bituminous to lignite may be successfully burned, and in addition other solid fuels such
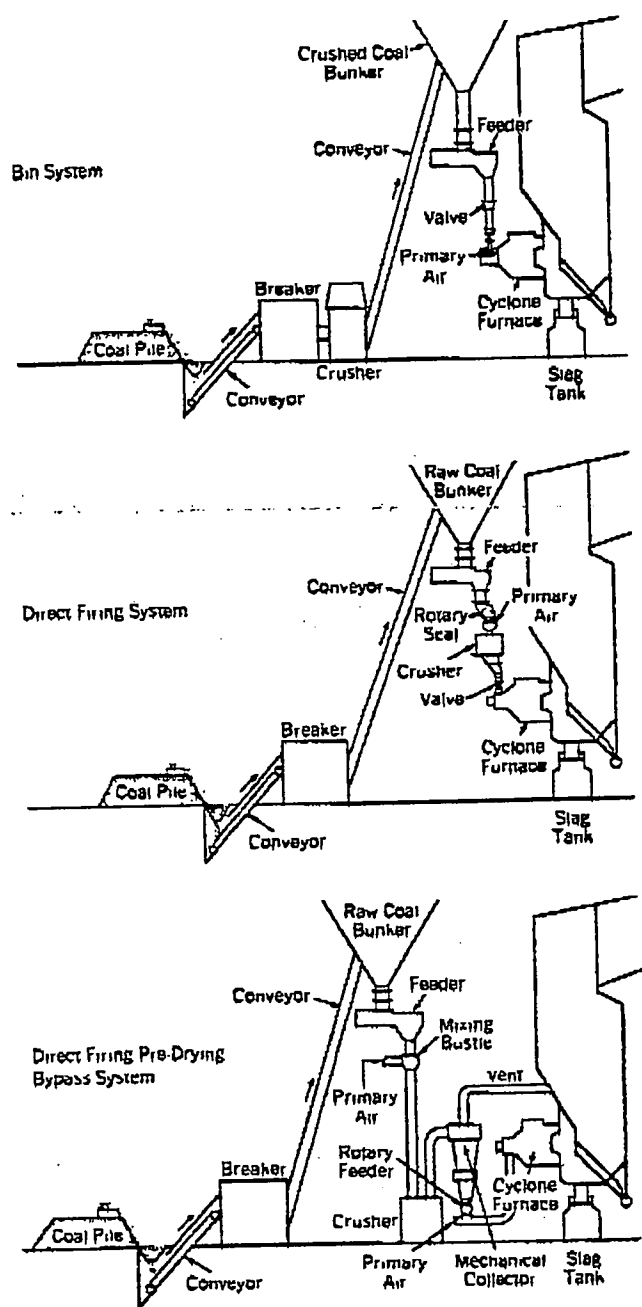

Fig. 2 Coal suitability for Cyclone Furnaces based on tendency to form iron and iron sulfide.

Fig. 4 Bin, direct-firing, and direct-firing pre-drying bypass systems for coal preparation and feeding to the Cyclone Furnace (schematic).

One of the two important criteria for coal suitability is the total amount of sulfur compared to the ratio of iron to calcium and magnesium (Fig. 2). This comparison gives an indication of the tendency of the coal to form iron and iron sulfide, both of which are very undesirable in the Cyclone Furnace. Coals with too high sulfur content and/or a high iron ratio are not considered suitable.

The other important criterion for establishing the suitability of coal for firing in the cyclone is the viscosity of the slag formed from the ash. Since satisfactory combustion of coal depends on the formation of a liquid slag layer in the cyclone, and since ash is removed from the cyclone and primary furnace in fluid form, the viscosity of the slag must permit slag flow at the temperatures experienced in the cyclone and primary furnace. Field experience with many different coals together with extensive investigation of ash characteristics has provided information for evaluating coal suitability, from a slag tapping standpoint, without actual firing tests.

Slag will just flow on a horizontal surface at a viscosity of 250 poises. The temperature at which this viscosity occurs (T_{250}) is used as the criterion to determine the suitability of a coal from this point of view. The T_{250} is calculated from a chemical analysis of the coal ash, and a value of 2600F is considered maximum (see Viscosity of Coal-Ash Slag, Chapter 15). Somewhat lower temperatures may be desirable for fuels with high moisture contents and low heating values.

The suitability of other solid fuels such as wood, bark, petroleum coke or chars must be considered on an individual basis and the amount of supplementary fuel carefully calculated.

Design features

Boiler furnace

The two general firing arrangements used for the Cyclone Furnace are one-wall firing and opposed firing. These are shown in Fig. 3. For smaller units, sufficient firing capacity is usually attained with Cyclone Furnaces located in only one wall. For large units, furnace width can often be reduced by using opposed firing.
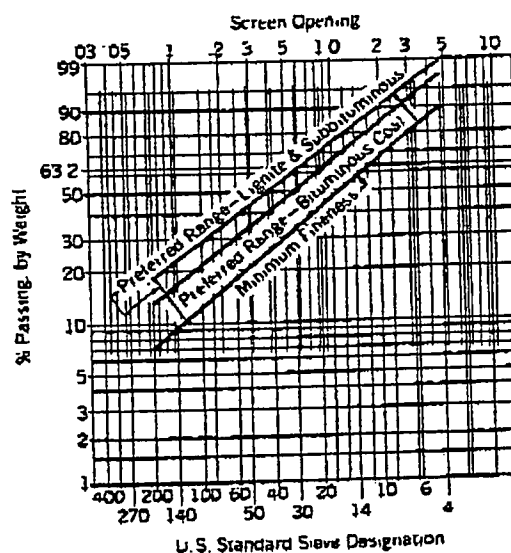
as wood bark, coal chars, and petroleum coke may be satisfactorily fired in combinations with other fossil fuels. Fuel oils and gases are also suitable for firing.

The suitability of coals is dependent on the moisture, ash and volatile contents of the coal together with the chemical composition of the ash. The volatile matter should be higher than 15 percent, on a dry basis, to obtain the required high combustion rate. The ash content should be a minimum of about 6 percent to provide a proper slag coating in the cyclone and can be as high as 25 percent on a dry basis. A wide range of moisture content is permissible depending on coal rank, secondary air temperature and fuel preparation equipment that may include capability for pre-drying the fuel.

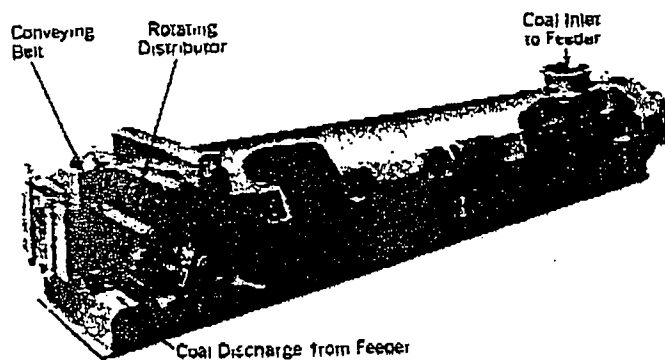Fig. 5 Sizing of crushed coal fired in the Cyclone Furnace.

Fig. 6 Belt-type coal feeder for the Cyclone Furnace.

Cyclone Furnace capacities

The size and number of Cyclone Furnaces used to fire a given boiler depend primarily on the boiler size and the load flexibility required. They are built commercially in sizes ranging from 6 ft diameter through 10 ft diameter, with an allowable maximum heat input per furnace of about 160 million to 425 million Btu/hr, respectively.

Coal preparation

There are two general types of coal preparation and feeding (see Fig. 4), the bin or storage system and the direct-firing system. The former is preferred for most bituminous coals when the plant layout permits. The range of sizing of crushed coal required with either system is given in Fig. 5.

With the bin system, coal is crushed in a central preparation plant to a size suitable for firing, and the crushed coal is delivered to the bunker. Because the crushed coal is relatively large in particle size, the hazards associated with pulverized-coal systems do not exist. The only precaution necessary is to provide adequate venting of the bunkers to assure removal of the small amounts of combustible gases released from freshly crushed coal of certain types. With the bin system there is less equipment in the boiler room, and short crusher outages can be accommodated without interrupting boiler operation.

The second method of coal preparation is the direct-firing system, which has a separate crusher located between the feeder and the burner of each Cyclone Furnace. The crusher is swept by hot air, and the intimate mixing of coal and hot air in the crusher helps to dry the coal. This improves crusher performance and ignition with high moisture coals. It is often easier to accommodate the direct-firing system in existing plants, where the coal handling equipment cannot readily be adapted to the bin system.

The direct-firing, pre-drying, bypass system (Fig. 4) is a variation of the second method, incorporating a mechanical dust collector between the crusher and the Cyclone Furnace. The collector is vented to the boiler furnace. This system is used when firing extremely high moisture coals. Its advantage is that moisture is removed from the coal during crushing and then vented to the boiler furnace instead of the Cyclone Furnace. This maintains maximum temperature in the cyclone with improved performance and slag tapping characteristics.
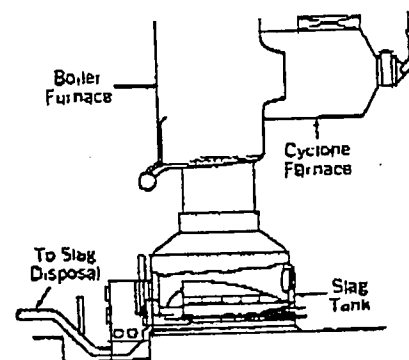

Fig. 8 Batch-removal slag-handling system for Cyclone-Furnace boiler.

Coal feeders

The coal feeders normally used are of the belt type, illustrated in Fig. 6. A rotating distributor is provided at the coal discharge from the feeder to assure a continuous and uniform rate of feed. This is necessary because the coal is burned almost instantaneously when it reaches the Cyclone Furnace, and fluctuations in feed are reflected in combustion conditions. The rapidity of combustion makes the Cyclone Furnace very responsive to load demands, and it has been demonstrated that boiler output can be made to respond very quickly to demand by changing coal-feeder speed. Continuous weighing devices can be applied to the belt feeder so that it can serve the dual function of coal scale and feeder.

Feeders of other types may also be used. Some are equipped with an angled cutoff plate at the coal discharge from the feeder to provide a uniform rate of feed.

Oil and gas burners

Oil and gas, as previously noted, are satisfactory cyclone fuels. These fuels can be burned at ratings and with performance equal to those with coal firing. Oil may be injected either into the secondary air stream or through the center of the front coal burner (see Fig. 7), where the oil is picked up and atomized by the high velocity air stream. Gas is fired through flat ports located in the
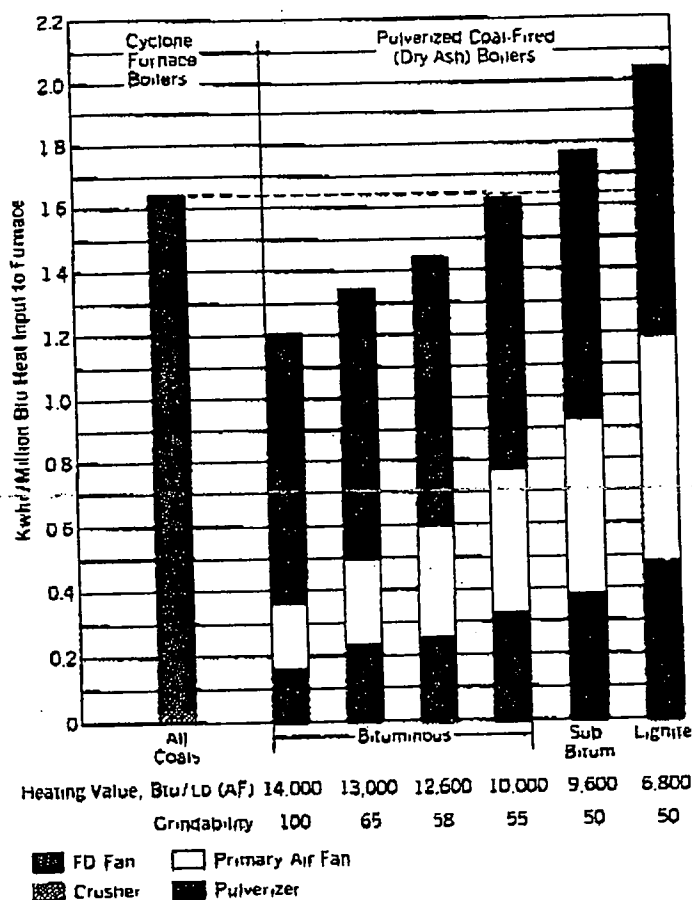

Fig. 7 Arrangement of gas and oil burner in Cyclone Furnace.

Fig. 9 Auxiliary power requirements of typical high-capacity pressure-fired Cyclone-Furnace and pulverized-coal units.

feeders are used, equal coal weights are obtained by maintaining equal feeder speeds. Where gravimetric type feeders are used, they measure and control the coal weights to the Cyclone Furnaces.

Combustion air flow is measured separately to each cyclone. Where individual ducts supply combustion air to individual cyclones, a venturi throat in each duct measures the air to each cyclone. Where cyclones are installed in a common windbox, secondary air flow is measured at the bell-mouth section of the secondary air port of each cyclone, then added to the primary and tertiary air flows of that cyclone. These flows are measured at orifices in the individual ducts.

Using these measurements, the controls maintain equal coal rates and air flows to each Cyclone Furnace. The overall excess air is controlled in the usual manner with a boiler meter based on steam flow and air flow. Oxygen recorders are usually provided as operating guides to monitor the controls.

Operating results

Fuels burned

The first commercial Cyclone-Furnace boiler was designed to burn Central Illinois coal and was installed at the Calumet Station of the Commonwealth Edison Company, Chicago, in 1944. Since then over 600 Cyclone-Furnace units have been installed in boilers throughout the United States and Europe. In this country coals of the following constituent range have been burned in commercial Cyclone-Furnace boilers:

Moisture, %	2 to 40
Volatile matter (dry), %	18 to 45
Fixed carbon (dry), %	35 to 75
Ash (dry), %	4 to 25

secondary air entrance to the cyclone. The gas burners and the oil burners located in the secondary air inlet may be left in place when coal is fired. This facilitates changing from one fuel to another by remote control without removal of the Cyclone Furnace from service. This feature makes the Cyclone Furnace most attractive for the firing of multiple fuels. However Cyclone Furnaces are not normally competitive with other firing methods unless coal is to be a principal fuel (see *Cyclone-Furnace Firing, Chapter 22*).

Slag handling equipment

Slag handling equipment for a Cyclone-Furnace boiler unit is similar to that for a pulverized-coal slag-tap unit. The capacity of the slag-handling equipment must be greater since the percentage of ash recovered in the Cyclone Furnace is higher. The batch-removal system, illustrated in Fig. 8, is the system generally used. Storage tanks into which slag is continuously tapped, quenched and accumulated are located under the furnace floor. Slag is withdrawn at intervals and discharged to a storage area, from which it may be removed at will (see *Design and Operation of Slag-Tap Units, Chapter 15*).

Combustion controls

Automatic combustion controls for Cyclone-Furnace boilers are generally based on maintaining equal coal weights and equal total air flows in the proper proportion to each Cyclone Furnace. Where volumetric type
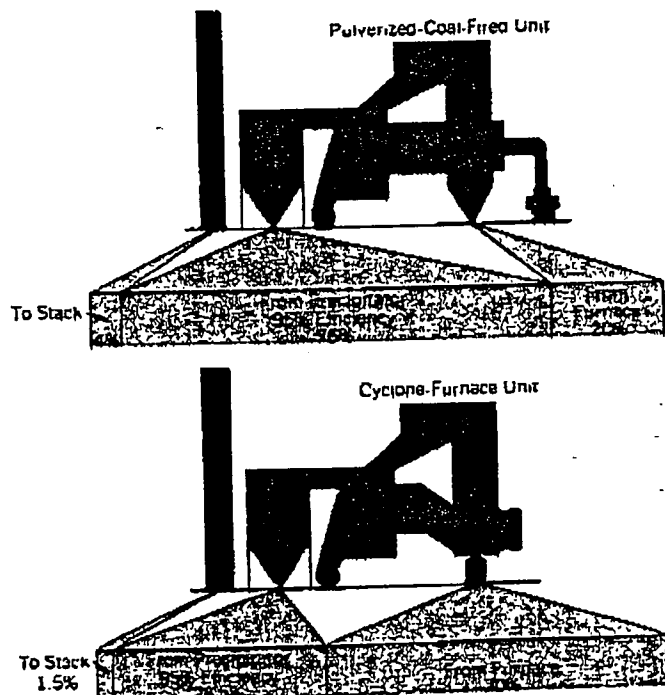

Fig. 10 Comparison of fly-ash emission from typical large dry-ash-removal pulverized-coal-fired unit and Cyclone-Furnace unit.

As mentioned previously, a number of by-products from petroleum and many waste fuels, such as bark, can be successfully burned. The petroleum products range in volatile matter from 5% for some petroleum coke to 60% for pitch. Because of the very low ash content of these petroleum by-products, it is usually necessary to add a slag-forming material or to mix the pitch with a coal having suitable ash characteristics to provide the necessary slag coating of the cyclone barrel. It may also be necessary to stabilize ignition of the low volatile coke by burning 5 to 10% auxiliary oil or gas.

Coal chars, resulting from the low-temperature carbonization of bituminous or lignitic coals having sufficient ash and volatile matter, are suitable for firing, provided the ash viscosity characteristics are suitable.

Two units designed to burn bark and bituminous coal in amounts up to approximately 50% by weight of each are in operation in a large Southern paper mill. To burn the bark successfully, it is necessary to fire sufficient coal to supply the slag coating in the cyclone and to maintain sufficiently high temperatures to provide the necessary fluidity of the slag. A chopper, or "hog", is used to reduce the bark to chips of a size suitable to the Cyclone Furnace. The chips are screened after "hogging" and oversize pieces are recycled.

Power requirements

Since the only coal preparation is crushing, the power required is low compared with that for pulverizing coal. To offset this, the forced draft fan power required is relatively high, Cyclone Furnace air pressure drop being in the range of 20 to 40 in. of water compared with 2 to 10 in. of water for pulverized-coal burners. Fig. 9 shows that the comparative power requirements vary considerably for different types of bituminous coals and lignite. For high-heating value, high-grindability bituminous coals, the Cyclone Furnace requires more power. However, for the low-heating value, low-grindability bituminous and lignite coals, for which the Cyclone Furnace is usually best suited, the power requirements are less than with pulverized-coal firing.

Combustion efficiency

The excess air required for satisfactory combustion of an individual Cyclone Furnace is less than 10 percent. However, where automatic controls are used and particularly where there are several Cyclone Furnaces for one boiler, excess air is usually maintained between 10 and 15% to assure that no individual cyclone is operating with insufficient air. When operating with coal of suitable sizing and with 10 percent excess air, the loss in efficiency from unburned combustible has been found to be less than 0.1 percent with most coals.

Ash recovery and dust collectors

The dust loading of the flue gas from coal-fired cyclone units is in the range of 20 to 30 percent of the ash in the coal, compared with about 80 percent for a dry-ash pulverized-coal-fired unit. This means that, if both units are equipped with 95 percent efficient precipitators or dust collectors, the ash discharged from the stack of a cyclone-fired unit will be less than half that from the stack of a dry-ash pulverized-coal-fired unit.

This comparison is illustrated in Fig. 10 for a large utility Cyclone-Furnace unit and a pulverized-coal unit arranged for dry ash removal. Both units are 600-megawatt capacity, each consuming approximately 7,000 tons of coal per day and producing 970 tons of ash. With pulverized-coal firing about 4 percent of the ash or 39 tons per day is discharged from the stack. Under similar operating conditions with the Cyclone-Furnace-fired unit only approximately 1.5 percent of the ash or 15 tons per day is discharged from the stack. On a Cyclone-Furnace-fired unit the fly ash collected in the precipitator may be returned to the Cyclone Furnace and recovered as slag. The slag from the furnace is chemically inert and disposal is relatively simple.

Typical Installations

Although Cyclone-Furnace units were first installed in central stations, their use has been extended to a wide variety of industries. Fig. 11 shows a unit installed in a large Northern industrial plant. The unit incorporates the bin system with one-wall firing. It is designed to produce 440,000 lb/hr of steam at 1350 psi and 905F superheat.

The designs of Cyclone-Furnace units have followed the general trend of the power industry to higher steam temperatures and pressures and larger capacities. Fig. 12 shows a Radiant boiler with one-wall firing. This unit produces 1,250,000 lb/hr of steam at 1900 psi and 1005F, with reheat to 1005F. Fig. 13 shows a Universal-Pressure once-through unit with opposed Cyclone-Furnace firing; the capacity of this unit is 6,000,000 lb of steam per hr at 3650 psi and 1003F, with 1003F reheat temperature.
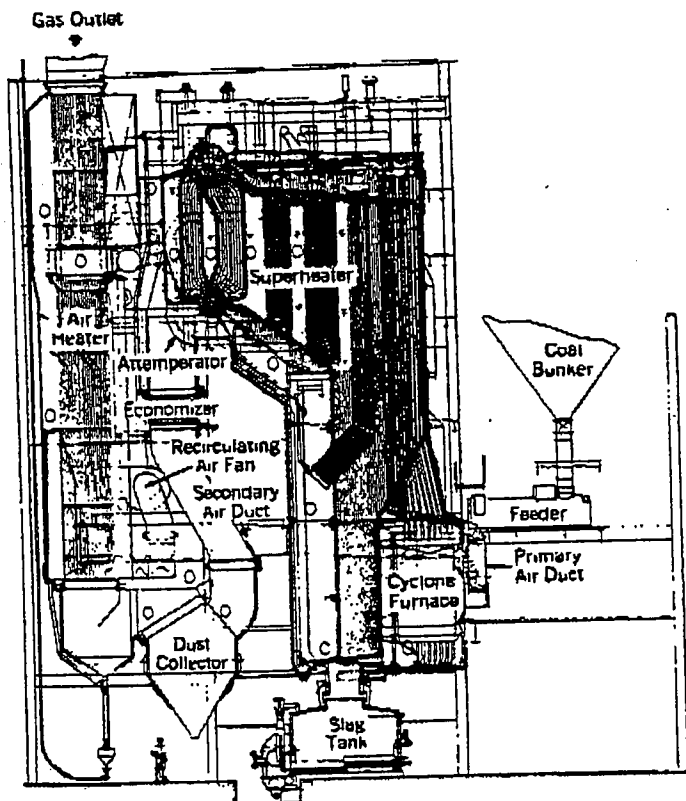

Fig. 11 Two-drum boiler with Cyclone Furnaces (one-wall) and bin system for coal preparation and feeding.

Steam / Cyclone Furnaces

Operation

Start-up

The Cyclone Furnace can be started by the continuous firing of coal, oil or gas. Coal is ignited by a permanently installed gas-lighting torch or a retractable oil-lighting torch inserted into the front of the secondary air port. With coal firing, the usual load range for good operation of an individual furnace is from 50 to 100% of rated capacity, depending on the ash characteristics; however, for short periods, such as start-up, loads of 20 to 25% can be carried with some increase in unburned combustible. The load range for continuous operation of the entire Cyclone-Furnace unit is from full to approximately half load, again depending on the ash characteristics and the furnace arrangement. For short periods such as overnight load drops, lower ratings can be carried by allowing the slag tapped from the Cyclone Furnace to accumulate and solidify on the boiler furnace floor. When the load is increased, this slag will melt and tap in the usual manner.

Maintenance

The principal items requiring maintenance are the coal crusher and the Cyclone-Furnace burner. Crusher maintenance includes replacement of hammers and grid bars at yearly or less frequent intervals, depending on the arrangement and the type of coal fired. In the burner, the coal is accelerated to the high velocity necessary to throw it against the slagged surfaces of the cyclone barrel. This high velocity causes erosion of the burner, which is minimized by the use of tungsten carbide or other erosion-resistant wear liners (Fig. 14). Since these liners normally last a year or more, they can be replaced or built up during regularly scheduled annual outages.
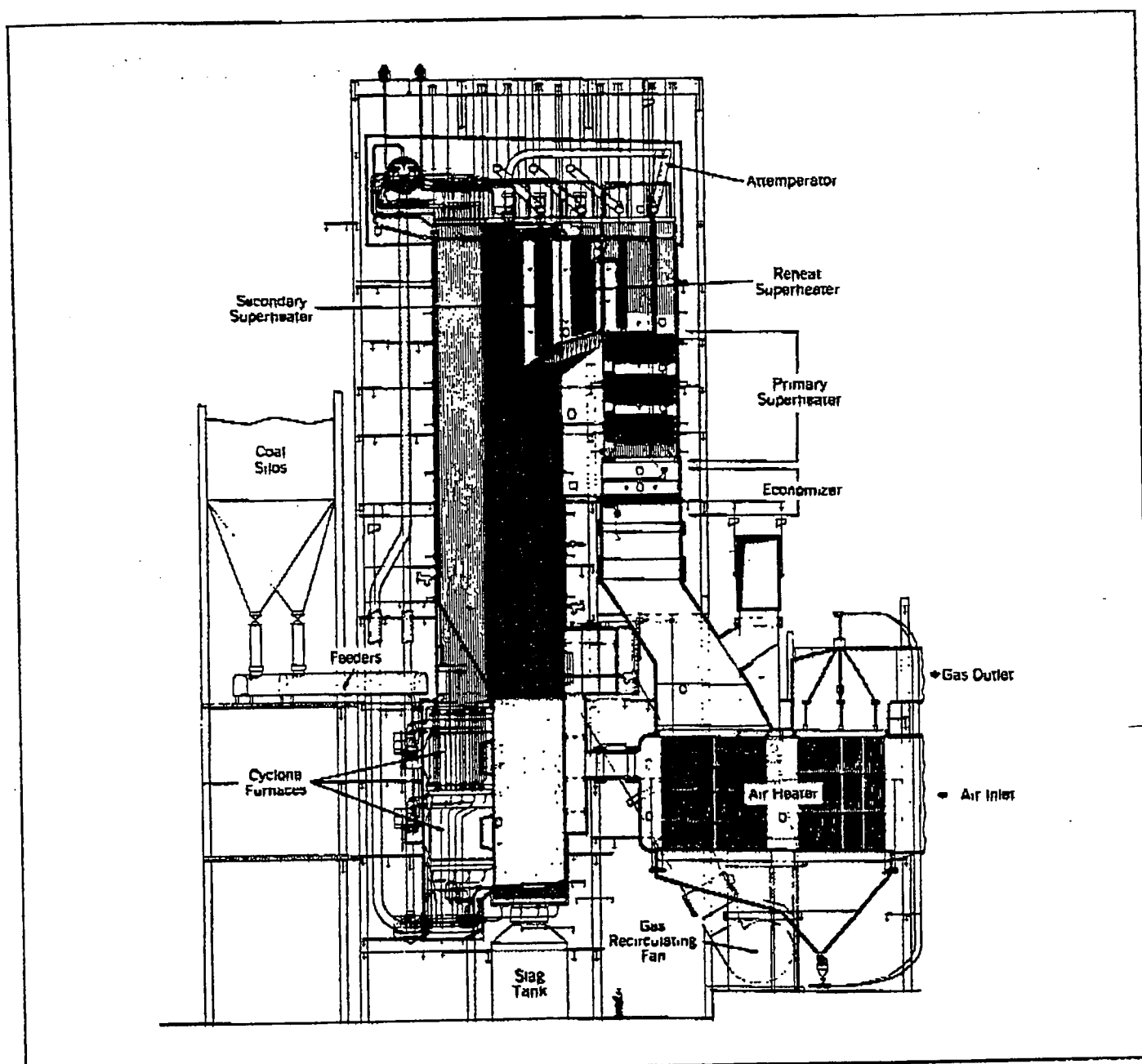

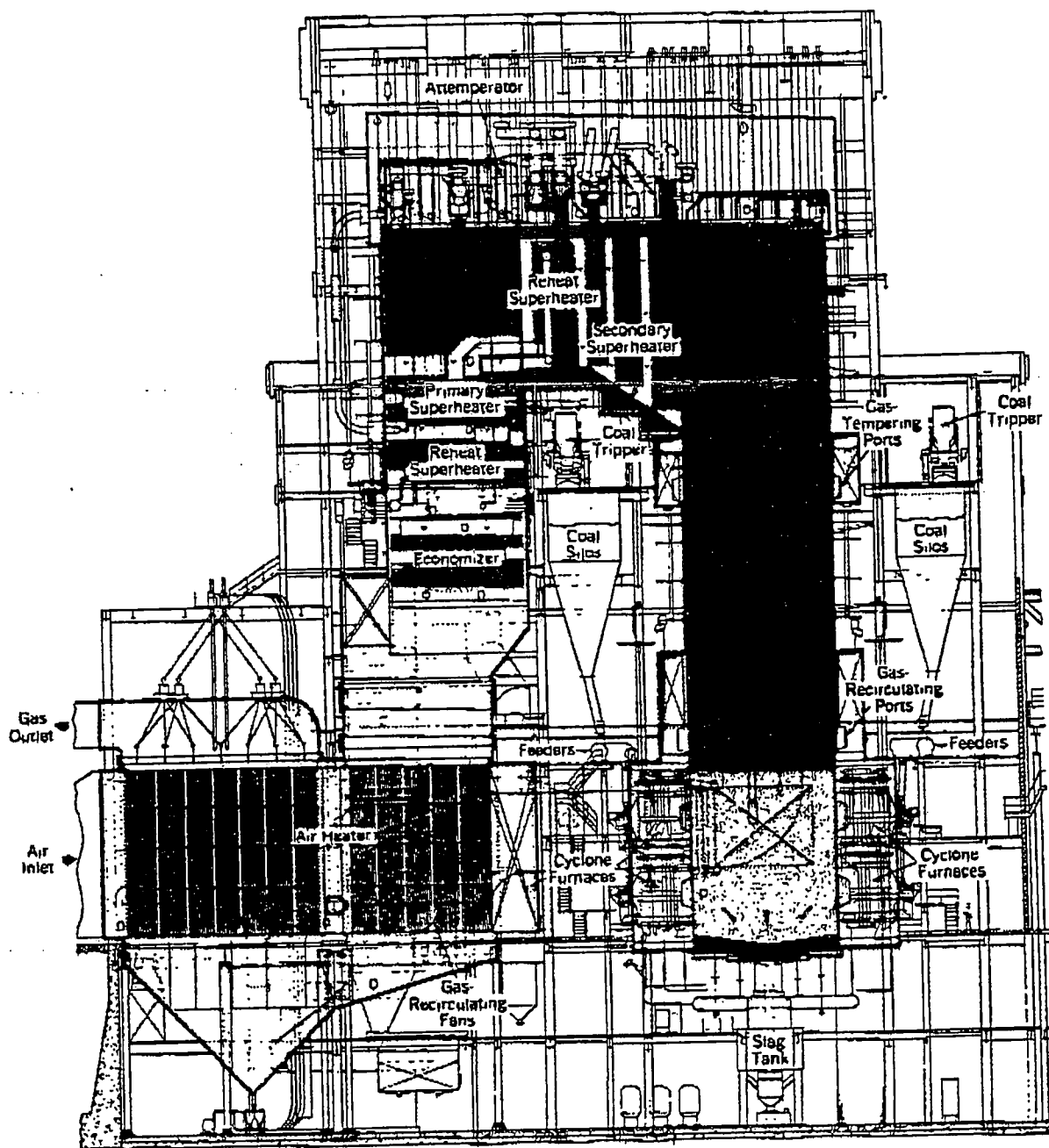Fig. 12 Radiant boiler with Cyclone Furnaces (one-wall) and bin system for coal preparation and feeding.

Fig. 13 Universal-Pressure boiler with opposed Cyclone Furnaces and bin system for coal preparation and feeding.

Summary

The Cyclone Furnace has made a significant contribution to the steam-power industry by improving combustion and furnace performance, by permitting the economic utilization of the lower grades and ranks of coal, and by alleviating the problems caused by coal ash. Because of this, it has gained wide acceptance in the U.S. and abroad. By 1970 about 700 Cyclone Furnaces were in service, under construction or on order for installation in the United States. These Cyclone Furnaces serve more than 150 boilers with a combined capacity of more than 200 million lb of steam per hr.

Fig. 14 Burner of Cyclone Furnace showing replaceable wear liners.

Chapter 15   Fuel-ash effects on boiler design and operation

From the beginning of the application of combustion of fossil fuels for the production of power, much attention has been devoted to the problems created by the residues of such combustion, broadly known as "ash." The complexity of these problems has increased with the size and rating of modern units. When burned, all but a few fuels have solid residues, and in some instances the quantity is considerable.

For continuous operation, removal of ash is essential to all methods of firing. In stoker firing with a fuel bed this is accomplished by the intermittent shaking or dumping of grate sections or by the continuous movement of the ash residue toward a point of discharge. In suspension firing the ash particles are carried out of the furnace by the gas stream or retained in part by settling or by adhering to boiler surfaces. Retained material of solid form is removed by periodic cleaning. If temperatures are sufficiently high, the retained ash is molten and may be drained continuously from the furnace. Some of the ash may form deposits of slag on the furnace walls (slagging), and a portion of the ash that is carried from the furnace by the flue gases may form deposits on the tubes in the gas passes (fouling). Also, under some conditions, the deposits may lead to corrosion of these surfaces. The nature and the amount of ash in the fuel to be used are, therefore, of major concern to the designer and the operator.

The following discussion is concerned primarily with the importance of coal ash in the design and operation of boilers, but consideration is also given to the importance of ash residue from petroleum fuels. Commercial fuels containing ash, and others with little or no ash, are listed in Table 1.

Some means must be provided to handle and dispose of the ash since ash in its various forms may seriously interfere with operation or even cause shutdown.

Ash content of coal

The ash content of coals varies over a wide range. This variation occurs not only in coal from different parts of the world or from different seams in the same region but also in coal from different parts of the same mine. Some rock and earthy materials find their way into the mined

product. Before marketing, some commercial coals are cleaned or washed to remove a portion of what would be reported as ash in laboratory determinations (see Chapter 8). In any case, the ash determinations of significance to the user are those made at the point of use, and the values noted below are on that basis.

The bulk of bituminous coal used for power generation in the U.S. has an ash content within the range of 6 to 20%. Low values of 3 or 4% are encountered infrequently, and such coals find other commercial uses, particularly in the metallurgical field. On the other hand, some coals may have an ash content as high as 30%. Many high-ash fuels are successfully burned in the Cyclone Furnace as well as in pulverized-coal-fired units. Their use is increasing in localities where the fuel costs indicate a favorable overall economy.

Nature of coal ash

The presence of ash is accounted for by minerals associated with initial vegetal growth or those which entered the coal seam from external sources during or after the period of coal formation. Appreciable quantities of inorganic material may be contributed to the commercial fuel by partial inclusion of adjacent rock strata in the process of mining.

Since quantitative evaluation of mineral forms is extremely difficult, the composition of the coal ash is

Table 1
Commercial fuels for power production

Fuels Containing Ash	Fuels Containing Little or No Ash
All coals	Natural gas
Fuel oil—"Bunker C"	Manufactured gas
Refinery sludge	Coke-oven gas (clean)
Tank residues	Refinery gas
Refinery coke	Distillates (most)
Most tars	
Wood and wood products	
Other vegetational products	
Waste-heat gases (most)	
Blast-furnace gas	
Cement-kiln gases	

Table 2
Ash content and ash fusion temperatures of some U.S. coals and lignite

Rank:	Low Volatile Bituminous	High Volatile Bituminous				Sub-bituminous	Lignite
Seam	Pocahontas No. 3	No. 9	Pittsburgh	No. 6			
Location	West Virginia	Ohio	West Virginia	Illinois	Utah	Wyoming	Texas
Ash, dry basis, %	12.3	14.10	10.87	17.36	6.6	6.6	12.8
Sulfur, dry basis, %	0.7	3.30	3.53	4.17	0.5	1.0	1.1
Analysis of ash, % by wt							
SiO_2	60.0	47.27	37.64	47.52	48.0	24.0	41.8
Al_2O_3	30.0	22.96	20.11	17.87	11.5	20.0	13.6
TiO_2	1.6	1.00	0.81	0.78	0.6	0.7	1.5
Fe_2O_3	4.0	22.81	29.28	20.13	7.0	11.0	6.6
CaO	0.6	1.30	4.25	5.75	25.0	26.0	17.5
MgO	0.6	0.85	1.25	1.02	4.0	4.0	2.5
Na_2O	0.5	0.28	0.80	0.36	1.2	0.2	0.6
K_2O	1.5	1.97	1.60	1.77	0.2	0.5	0.1
Total	98.8	98.44	95.74	95.20	97.5	86.4	84.3
Ash fusibility							
Initial deformation temperature, F							
Reducing	2900+	2030	2030	2000	2060	1990	1975
Oxidizing	2900+	2420	2265	2300	2120	2190	2070
Softening temperature, F							
Reducing		2450	2175	2160		2180	2130
Oxidizing		2605	2385	2430		2220	2190
Hemispherical temperature, F							
Reducing		2480	2225	2180	2140	2250	2150
Oxidizing		2620	2450	2450	2220	2240	2210
Fluid temperature, F							
Reducing		2620	2370	2320	2250	2290	2240
Oxidizing		2670	2540	2610	2460	2300	2290

customarily determined by chemical analysis of the residue produced by burning a sample of coal at a slow rate and at moderate temperature (1350F) under oxidizing conditions in a laboratory furnace. It is thus found to be composed chiefly of compounds of silicon, aluminum, iron, and calcium, with smaller amounts of magnesium, titanium, sodium and potassium. The analyses of coal ash in Table 2 indicate what may be expected of some coals from various areas of the United States. A comparison of analysis of ash from wood and from two low-ash-content lignite coals is indicated in Table 3. The ash analyses do not always total 100%, since the analysis does not include all constituents.

The element sulfur is present in practically all coal, and its effect on equipment performance has been given much attention. Sulfur itself burns as a fuel with a relatively low heating value (3980 Btu/lb when burned to SO_2), but its reputation, which is nearly all bad, results from the effect of its chemical combination with other elements. Under certain conditions some of these compounds corrode boiler components; others contribute to the fouling and slagging of gas passages and heating surfaces.

Some of the sulfur in coal is in combination with iron as FeS_2. Sulfur may also be present in the form of complex organic compounds and, in minor amounts, in combination with the alkaline earths (calcium and magnesium). When the fuel is burned, the sulfur compounds are normally converted to more or less stable mineral oxides and sulfur dioxide gas, SO_2. A very small part of the SO_2 thus formed is further oxidized to SO_3. These sulfur gases are carried along with the other combustion gases, and their presence, under certain conditions, can contribute to corrosion of boiler heating surfaces and to air pollution problems (Chapter 18).

Table 3
Comparison of ash from two lignites with wood ash

	Lignite-Type Ash		Wood Ash
Ash, dry basis, %	5.0	6.0	1.0
Sulfur, dry basis, %	1.0	1.0	0.1
Analysis of ash, % by wt*			
SiO_2	17.9	18.9	33.8
Al_2O_3	13.2	19.5	2.6
TiO_2	0.5	0.6	0.2
Fe_2O_3	6.0	6.4	1.6
CaO	59.7	40.8	56.5
MgO	2.0	12.7	4.7
Na_2O	0.2	1.0	0.5
K_2O	0.5	0.1	0.1
Total	100.0	100.0	100.0
Ash Fusibility—Hemispherical Temperature, F			
Reducing	2680	2470	2580
Oxidizing	2650	2470	2550

* Adjusted to 100%

Coals may be classified into two groups based on the nature of their ash constituents. One is the bituminous-type ash and the other is the lignite-type ash. The term "lignite-type" ash is defined as an ash having more CaO plus MgO than Fe_2O_3. By contrast, the "bituminous-type" ash will have more Fe_2O_3 than CaO plus MgO.

Locations of U.S. deposits of coals are shown in Fig. 2, Chapter 5. The coal fields labeled "bituminous-type ash" include all those of Triassic age and older coals The fields shown for "lignite-type ash" include all those of Jurassic age and younger coals, and all ranks of coals in these deposits.

Ash fusibility

The preferred procedure for the determination of ash fusion temperatures is outlined in ASTM Standard D-1857. Earlier procedure used only a reducing atmosphere for ash-fusibility determination whereas the standard adopted in 1968 offers the use of both reducing and oxidizing atmospheres. The previous method had loosely defined softening and fluid critical points; the new procedure uses improved definitions, as follows:

Initial deformation temperature, at which the first rounding of the apex of the cone occurs.

Softening temperature, at which the cone has fused down to a spherical lump in which the height is equal to the width at the base.

Hemispherical temperature, at which the cone has fused down to a hemispherical lump at which point the height is one half the width of the base.

Fluid temperature, at which the fused mass has spread out in a nearly flat layer with a maximum height of one-sixteenth in.

The determination of ash fusion temperatures is strictly a laboratory procedure, developed in standardized form, which experience shows can be duplicated with some degree of accuracy. For example, the permissible differences of reproducibility between two furnace runs may range from 100 to 150F. However, some bituminous-type ash, containing relatively large amounts of silica, may exhibit low ash-softening temperatures, yet exhibits high viscosity characteristics in its plastic range. Some lignite-type ash, containing large amounts of calcium and magnesium, may react with the refractory base (kaolin and alumina), or it may evolve gaseous products and swell, thereby causing changes in density of the ash cone. Methods for determining fusibility of coal ash used by countries outside the U.S. may also vary considerably. Thus, ash fusibility data should be used with care and its limitations recognized.

Ash melts when heated to a sufficiently high temperature. Following combustion, individual ash particles are generally in the form of tiny spheres (cenospheres) that appear hollow when viewed under a microscope, as illustrated in Fig. 1. The form of the ash particles indicates that, during combustion of the coal, the particles were actually liquid and the spheres were formed as tiny bubbles by evolved gases trying to escape. What happens to these particles depends on their physical and chemical characteristics and on furnace conditions If
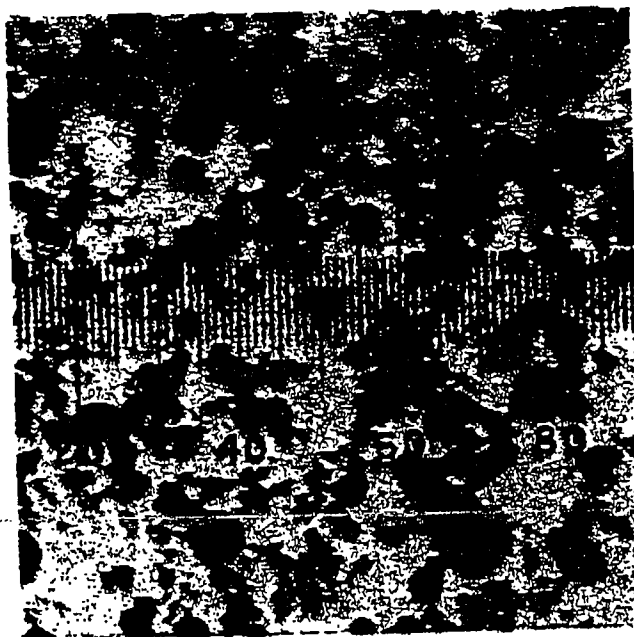

Fig. 1 Ash cenospheres (485x) formed in burning pulverized coal.

cooled promptly and sufficiently, the result is a dusty ash that may travel through the equipment, lodge on heating surfaces, drop out in soot hoppers and along flues, or collect at the base of the stack. Those particles that remain in suspension are carried out with the flue gases to the particulate-removal equipment (Chapter 18) and stack.

The individual ash particles do not, however, always cool quickly to a solid state. If insufficiently cooled, they remain molten or sticky and tend to coalesce into large masses in the boiler furnace or other heat-absorption surfaces. This problem is dealt with by adequate design of burners and furnace arrangement for the fuels to be burned and by proper attention to boiler operation.

Viscosity of coal-ash slag

Viscosity of coal-ash slag is measured in a high-temperature rotating-bob viscometer (Figs. 2 and 3), similar to one originally developed by the U.S. Bureau of Mines. The control panel is shown at the left in Fig. 2 and the furnace with its measuring element is at the right. A section through the furnace is shown in Fig. 3. The molten-slag sample is placed in a platinum crucible. There is an optical electronic device for measuring the torsional deflection of the calibrated wire, and the torque is recorded on a chart. Provision is made for controlling the atmosphere within the furnace.

Ash is introduced into the crucible at an elevated temperature (2600-2800F) and held at that temperature until it becomes uniformly fluid and all decomposition gases have been expelled. The temperature is then decreased in predetermined steps, and the viscosity is measured at each temperature.

Measurement of viscosity of coal-ash slags provides reliable data that can be used for determining suitability of coals for use in slag-tap type boilers. Since viscosity measurements require a considerable amount of coal ash that may not be readily available and, in addition,
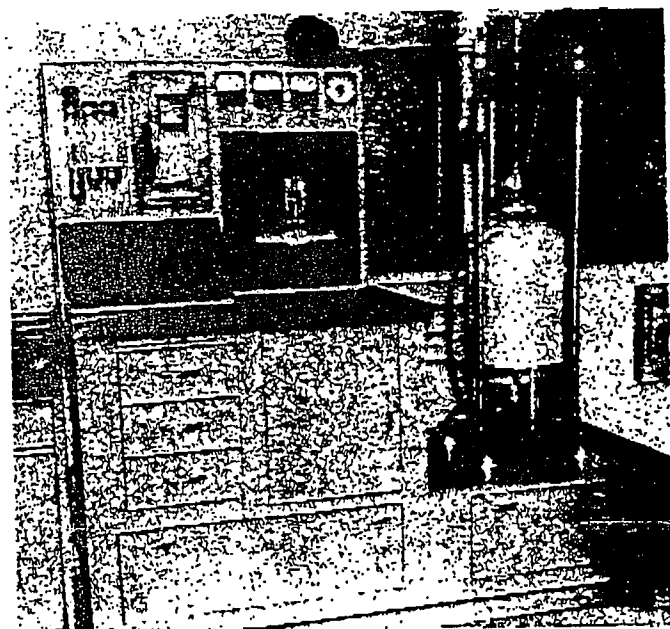
Fig. 2 High-temperature viscometer for determining the vis-cosity of molten coal ash.

are costly and time consuming, it is desirable to calculate viscosity from chemical analysis of the coal ash. It has been feasible to remove liquid slag from operating furnaces for slags having a viscosity at or below 250 poise. A reasonable temperature limit, to provide ample reduced load operation, has been found to be 2600F. Thus, a dependable guide for suitability of coal-ash slag may be referred to as the T_{250} or the temperature in degrees F to obtain a 250-poise viscosity.

Fig. 3 Section through furnace of high-temperature viscometer.

Laboratory studies and field investigations, supplementing investigations by the Bureau of Mines, resulted in a calculation method for determining the T_{250} of slag from coals in the eastern United States. This method employs the ash fusibility (hemispherical temperature) in a reducing atmosphere and the "silica ratio" of the coal, where the

$$\text{Silica ratio} = \frac{SiO_2 \times 100}{SiO_2 + Fe_2O_3 + CaO + MgO}$$

The use of this method is illustrated in Fig. 4 where the T_{250} is obtained by entering with the silica ratio and the hemispherical temperature in a reducing atmosphere plus 200F. For example, for a coal ash having a silica ratio of 62 and a hemispherical temperature of 2300F, locate this point at the intersection of the 2500F line and the 62 silica ratio. From this point extend a straight line at a 10-degree slope from the vertical to the 250-poise value; this slag thus has a calculated T_{250} of 2450F.
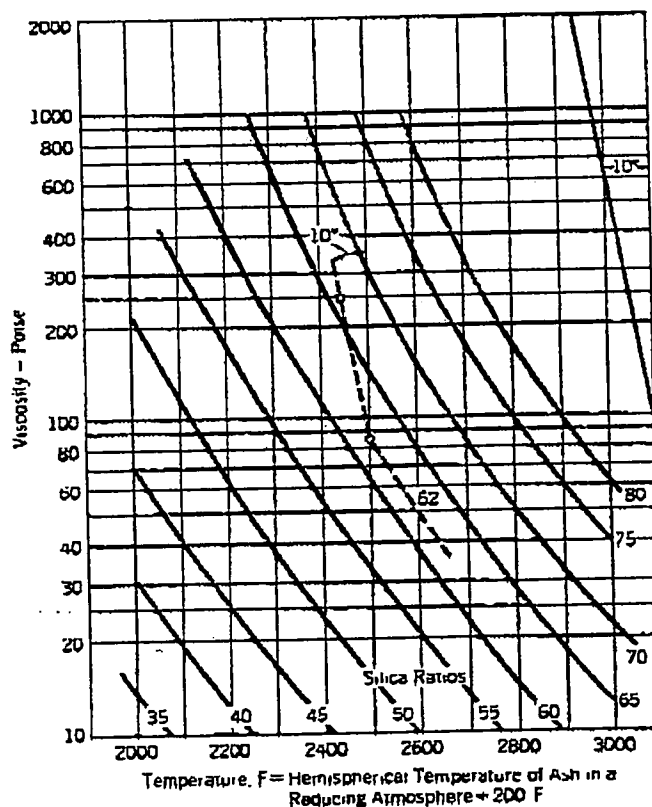

Fig. 4 Slag viscosity from ash analysis.

The constituents of a coal ash can be classed as either basic or acidic. Basic constituents are the Fe_2O_3, CaO, MgO, Na_2O, and K_2O; the acidic constituents are SiO_2, Al_2O_3 and TiO_2. Laboratory studies have shown that the relative amounts of the basic and acidic constituents in the ash can be used as a means of predicting the viscosity of the slag (see Fig. 5). The viscosity of a slag decreases as the base-to-acid ratio increases to 1.0 where

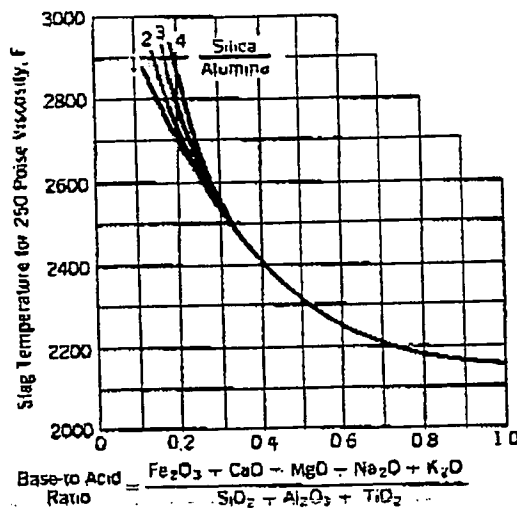$$\text{Base-to-acid ratio} = \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O}{SiO_2 + Al_2O_3 + TiO_3}$$

Fig. 5 Plot of temperature for 250-poise viscosity vs base-to-acid ratio—based on a ferric percentage of 20.

This correlation takes into account the SiO_2 to Al_2O_3 ratio which has an effect with slags having a low base-to-acid ratio. For bituminous-type coal ash and for lignite-type ash having an acidic content in excess of 60%, the base-to-acid ratio method is used in preference to the silica-ratio method to estimate the T_{250}.

For coals with lignite-type ash and an acidic content less than 60%, the dolomite percentage method is used (see Fig. 6).

Dolomite percentage =
$$\frac{(CaO + MgO)100}{Fe_2O_3 + CaO + MgO + Na_2O + K_2O}$$

where the sum of the basic and acidic constituents is adjusted to equal 100%.

Effect of iron on ash behavior

Coals having bituminous-type ash usually contain iron and its compounds as a principal component; the iron may exist in more than one state, i.e., metallic (Fe), ferrous (FeO) or ferric (Fe_2O_3). The Fe_2O_3 reported in an analysis of ash is actually the equivalent Fe_2O_3 representing the sum of Fe, FeO and Fe_3O_3 expressed as Fe_2O_3. Experience indicates that iron has a dominating influence on the behavior of ash in the furnace, as indicated by its effect on the ash softening temperature.

The specific effect of iron in coal ash is interesting. In completely oxidized form (Fe_2O_3) iron tends to raise all four values of ash fusion temperatures, initial deformation, softening, hemispherical and fluid, while in the lesser oxidized form (FeO) it tends to lower all four of these values. The effect of iron, in each of the two forms, on initial deformation and hemispherical temperatures is indicated in Fig. 7 plotted for a large number of ash samples from U.S. coals. Data in Fig. 7 show that as the amount of iron in the ash increases there is a greater difference in ash fusibility between oxidizing and reducing conditions. This effect may be negligible with coal ash containing small amounts of iron. Lignite-type ash generally contains small amounts of iron and the ash fusion temperatures are affected

very little by the state of oxidation of the iron in the slag. In fact, lignite-type ash having a high basic content and high dolomite percentage may have ash fusion temperatures that are lower on an oxidizing basis than a reducing basis. Ash hemispherical temperatures and ash analyses of lignites appearing in Table 3 illustrate this effect.

The iron content of a slag and the degree of oxidation of the iron also have a great influence on the viscosity of the slag. The degree of iron oxidation is normally expressed as the ferric percentage where

$$Ferric\ percentage = \frac{Fe_2O_3 \times 100}{Fe_2O_3 + 1.11FeO + 1.43\ Fe}$$

In stating the viscosity of a slag containing a significant amount of iron, it is important that the degree of oxidation, or ferric percentage, be expressed. Experience indicates that slags from boiler furnaces operating under normal conditions have an average ferric percentage of 20. The curves appearing in Fig. 5 are based on a ferric percentage of 20. Fig. 8 shows viscosity curves for a typical slag with various stages of oxidation of the iron. For coal ash having small amounts of iron, such as a lignite-type ash, this effect will be greatly diminished.

Furnace design

A properly designed furnace has two functions: (1) to burn the fuel completely and (2) to cool the products of combustion sufficiently so that the convection passes of the boiler unit may be maintained in a satisfactory condition of cleanliness, with a reasonable amount of sootblowing (see also Chapter 12). The products of combustion include all the impurities either in the solid, liquid or gaseous state. Experience and tests indicate that when the average gas temperature leaving a coal-fired furnace is too high, the ash particles are molten or
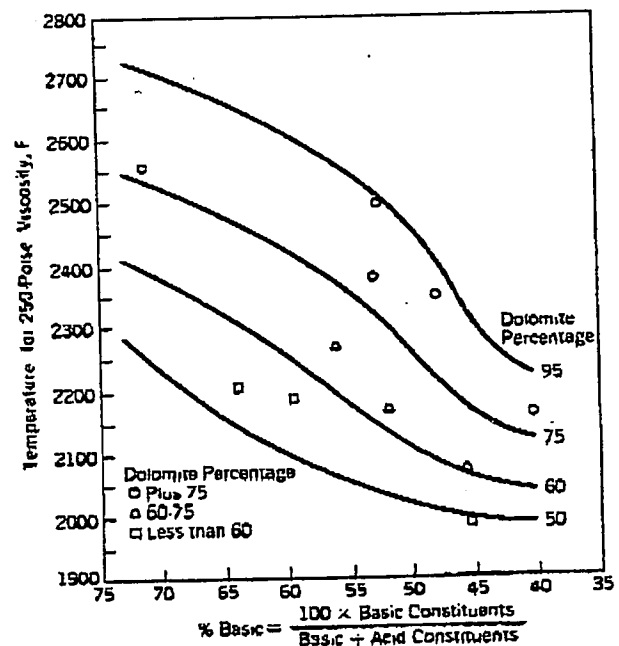

Fig. 6 Basic content and dolomite percentage of ash vs temperature for 250-poise viscosity.
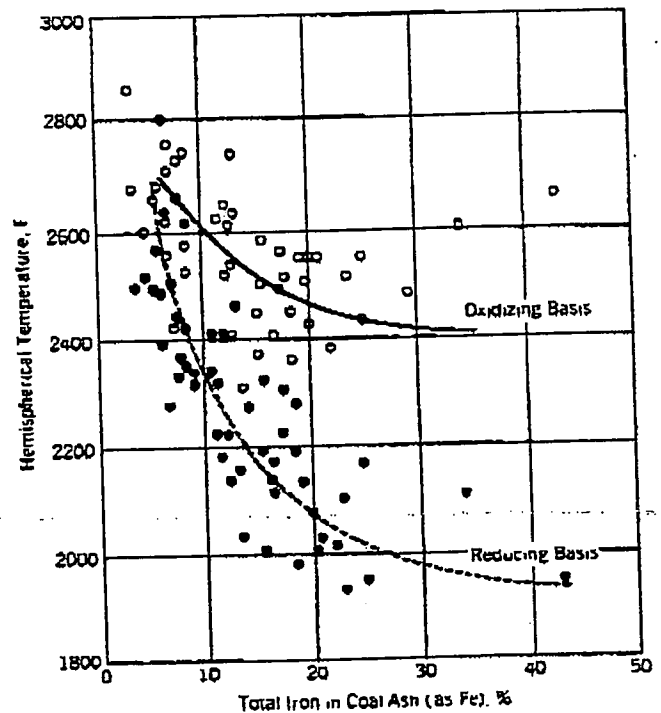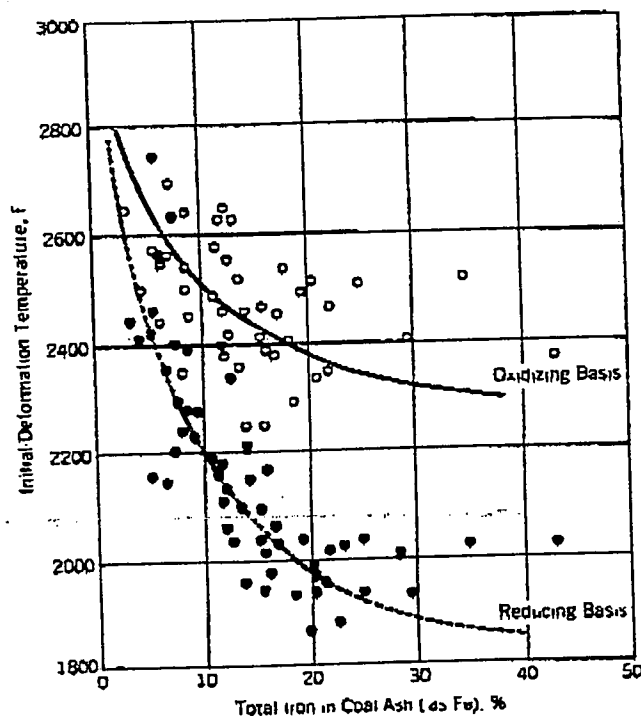
Fig. 7 Influence of iron on coal ash fusion temperatures.

sticky, and the need for cleaning the ash deposits from the upper-furnace and high-temperature zones in the convection passes may become excessive. This is, of course, subject to some latitude, because what constitutes excessive cleaning depends largely on the opinions of the individual operating crews.

In establishing the proper functional design of a furnace, two methods of cooling the products of combustion must be considered, namely, radiation and gas tempering.

Cooling gas by radiation

For many years the method used to cool the products of combustion has been that of providing radiant furnace-cooling surface. Sufficient surface is installed to assure a reduction in gas temperature to a level where convection passes can be kept reasonably clean. There is a general relationship between the average desired furnace-exit-gas temperature and the slagging and fouling potential of the coal ash. There can be a considerable variation in the gas temperature at the furnace outlet (see Furnaces, Chapter 4) and the maximum gas temperature can be considerably higher than the average. The usual design criterion of furnace size when using this method of cooling gases is "heat release rate," which is defined as heat available per hour per sq ft of equivalent flat projected water-cooled furnace enclosure surface (see Chapter 4).

Heat available, in turn, is defined as the amount of energy released in the furnace and available for increasing the temperature of the products of combustion. It is equal to (heat input in fuel + heat in air) − (heat required to evaporate moisture in fuel + ½ radiation loss). The assumption that half of the radiation loss occurs from the furnace is an acceptable approximation.

The relationship between furnace release rates and furnace-exit-gas temperatures has been developed from field test data. Factors affecting this relationship include type of furnace design, method of firing, fuel, burner location, burner input, and furnace wall construction.

From information obtained over a number of years, desirable heat release rates have been established for different types of coals. In general, units using coals having low or medium ash-slagging tendencies can have
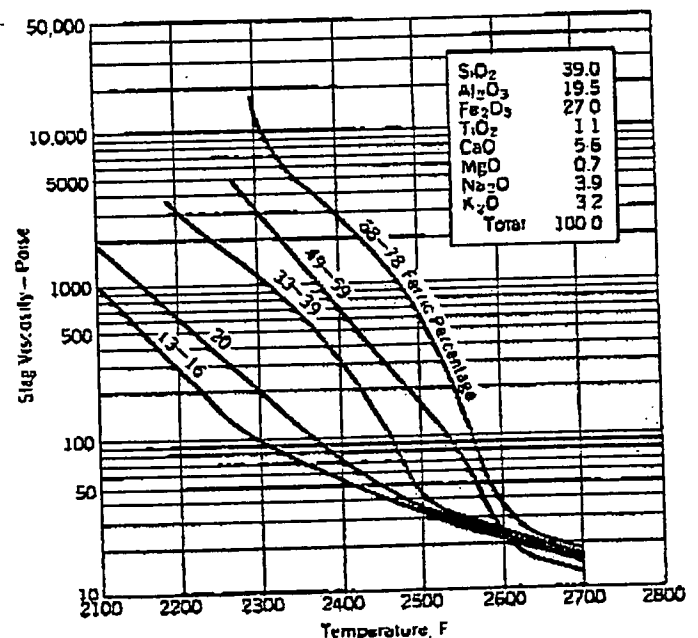

Fig. 8 Viscosity-temperature plots of a typical slag showing effect of ferric percentage.

the highest heat release rates. A boiler designed to burn this type coal is shown in Fig. 9. Units using coals having high or severe ash-slagging tendencies will require furnaces with heat release rates about 10 to 15% lower. Units designed for some very severe ash-slagging coals, such as North Dakota lignites, may require furnace heat release rates reduced by 30% as compared with furnaces designed for low- and medium-slagging-type coals.

With current use of high-volume type train shipments, coal from one source only may be considered for the life of the power plant; it may be shipped, for example, from northern West Virginia to New England. Thus, for best overall operation, units should be designed for the ash characteristics of the coal to be fired.

Furnaces fired with oil are generally designed for high heat release rates. Convection-pass tube spacing can be set in design so as to overcome ash-deposition problems when high-ash oils are fired. With these high heat releases, designs must take into consideration economic factors of tube metals, furnace proportions and high-temperature corrosion.

Gas tempering

The second method of cooling hot furnace gas is that known as "gas tempering," in which relatively cool gas from the economizer outlet is mixed with the hot furnace gas near the furnace outlet (Figs. 9 and 10). The tempering gas supply is normally taken from the top of the main gas-recirculation duct. Gas recirculation for superheater control is discussed in Chapter 12.

Gas tempering provides the operator with a control of furnace-exit-gas temperature with little or no effect on superheater and reheater absorption. Thus, if a high-fouling type coal is fired, the amount of tempering gas is increased to lower the gas temperature leaving the furnace to a level at which the convection surface is free from fouling. On the other hand, if a low-fouling type coal is fired, the amount of tempering gas is decreased, thereby reducing fan power. With some coals, tempering may be reduced to zero where experience indicates that it is not needed.

Gas tempering thus provides a positive means of controlling gas temperature at the furnace outlet. With this method of design, furnaces may be held to a reasonable height. Overall building requirements, steam piping, structural steel, and platforms are all decreased with no sacrifice in quality or performance of equipment. Rather, performance has been upgraded, since the gas temperature leaving the furnace is subject to positive control and is not dependent on furnace cleanliness. When gases are cooled only by radiation, the upper furnace cooling surfaces may be covered with slag from low-fusion coal and will not do the required cooling.

With gas tempering, the combustion gases are cooled uniformly across the width of the furnace, minimizing the large temperature variation customary with older designs. The possibility of localized slagging and fouling and excessive superheater-metal temperatures is therefore reduced.

With high steam temperatures and pressures it may be necessary to resort either to steam-cooling the walls or locating steam-cooled surface in high gas-temperature zones in the furnace subject to radiant heat. Gas temper-

ing eliminates these requirements in most cases, and thus improves the reliability and availability of units.

Gas tempering reduces the furnace height required to obtain an equivalent furnace-exit-gas temperature. The Universal-Pressure boiler (Fig. 10), has operated successfully with dry-ash removal with a furnace-exit-gas temperature of 2210F and 20% gas tempering at full load.

Gas tempering permits engineers to design high-capacity units that occupy less space and have greater reliability, lower maintenance, safer operation, and reduced overall plant costs.

Ash from pulverized-coal firing

No matter how fine the pulverization, the fuel fed to the furnace still has all its original ash. However, the final ash product ejected from a pulverized-coal-fired unit differs in appearance from the refuse of a stoker-fired unit. With pulverized coal, nearly all the ash particles are formed in suspension and tend to remain in suspension in a dry-ash furnace, with the individual particles well dispersed and very much smaller than those from spreader-stoker firing. In the slag-tap furnace, a portion of the ash particles coalesces on walls or other suitably designed surfaces and drains to the furnace bottom.

When pulverized coal is burned in a dry-ash furnace (e.g., Fig. 10), about 80% of the ash originally in the coal leaves the furnace entrained in the flue gas. On the other hand, with pulverized coal burned in a slag-tap furnace, as much as 50% of the ash may be retained in the furnace. The other 50% of total ash in the coal leaves the unit in the form of dust. With the Cyclone Furnace 70 to 80% of the total ash is retained, and only 20 to 30% leaves the furnace as dry ash in the flue gas (see *Ash Recovery and Dust Collectors, Chapter 10*). Particulate-removal equipment is placed ahead of the stack to prevent the ejection of large quantities of this ash to the atmosphere (Chapter 18).
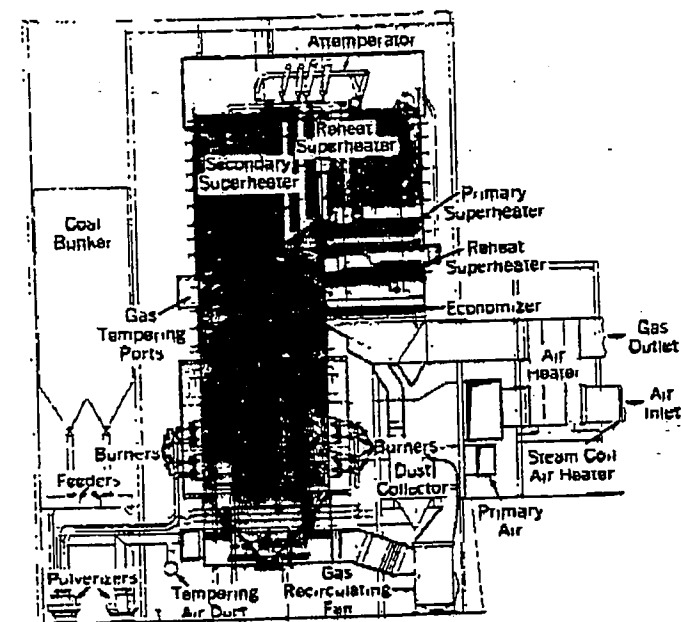

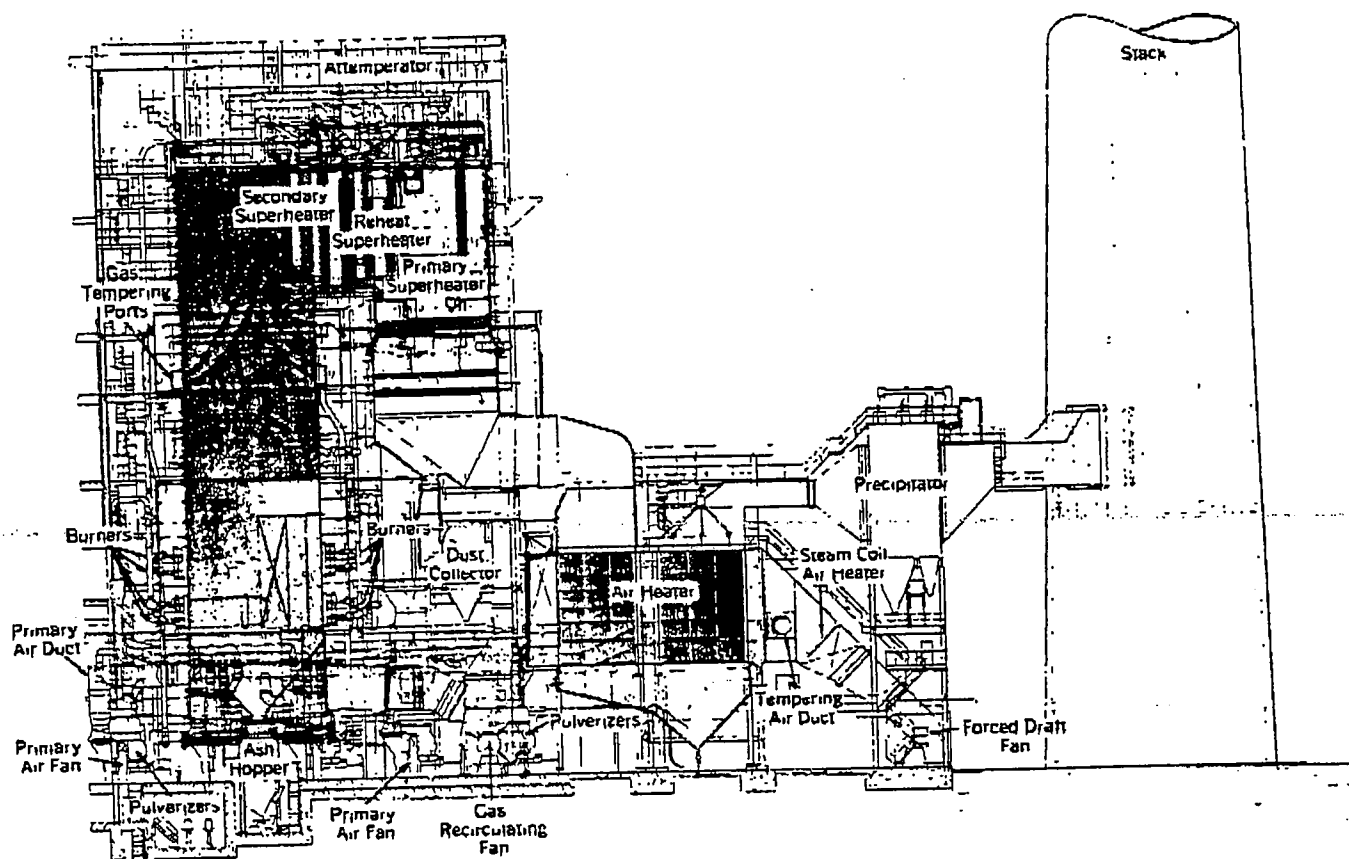**Fig. 9** Universal-Pressure boiler with gas tempering in front wall.

Fig. 10 Universal-Pressure boiler with gas tempering in front and rear walls.

Ash produced by stokers

In the fuel bed of a stoker, whether of the spreader, underfeed, or chain-grate type, ash particles tend to become fused together. In a properly operating stoker burning a suitable coal, the passage of air and the agitation of the fuel bed serve to keep ash accumulations more or less porous, and the ash is discharged to an ashpit in fairly large pieces varying from popcorn size upward.

Not all the ash is retained in a fuel bed. With the types of stokers mentioned, and particularly the spreader stoker, some of the fuel is burned in suspension. A considerable quantity of ash particles, containing some unburned and some still-burning fuel, is consequently carried over with the gases. With the spreader stoker this material is usually collected in hoppers provided for the purpose and is reinjected into the furnace for further burning of any combustible that it may contain (see Chapter 11). Reinjection is also used occasionally with other types of stokers.

Use of dry-ash or slag-tap units

Considered answers to the following pertinent questions relating to fuel are essential in initiating the design of a successful coal-fired unit:

1. Has the particular coal selected been burned extensively, so that its combustion and ash characteristics are well known?
2. Will the source of coal and the characteristics of the coal remain substantially constant during most of the life of the equipment. What is likely to be the "worst" fuel supplied?
3. What auxiliary fuel may be made available during periods of temporary suspension of coal delivery?
4. What type of equipment is best suited to the experience of the operating personnel?
5. In the public interest, for better public relations, or to comply with civil regulations, what is required to limit atmospheric pollution from dust?
6. What method of final refuse disposal is available?

Answers to these questions make it possible to select proper equipment for the specific method of utilizing the coal. For instance, coal should not be burned in a slag-tap furnace if the ash fusion temperature and viscosity are higher than experience indicates they should be for successful tapping. Slag-tap furnaces are rarely suitable for an ash viscosity greater than 250 poise at 2600F. If the ash viscosity of the coal selected is too high or marginal, equipment permitting the ash to be removed in dry form is indicated.

Ash erosion

Ash erosion must not be ignored even though coal-ash particles may be exceedingly fine. Where ash particles are concentrated in a local region, such as in a gas turn, erosion is a potential problem. The induced draft fan is a well-known example, and erosion is an important fac-

tor to be considered in selecting the type of fan and its performance characteristics. Blade wear is relatively low at fan-blade-tip speeds under 22,000 ft/min. Above this tip speed the wear from erosion increases very rapidly and higher speeds should not be considered in designs having a high concentration of entrained ash. Local high concentrations of ash through the boiler setting may cause erosion of highly critical pressure parts. This action is liable to be found where ash tends to concentrate in streams, as at turns formed by baffles within boiler banks. In this case the remedy is to limit gas velocities and to eliminate baffles if possible. The elimination of baffles has been the trend in the development of coal-fired boiler units, as illustrated in Fig. 11, where the gas flow continues horizontally through the tube banks without turns. Maximum allowable gas velocities with various fuels are given in Table 4.

Table 4
Design gas velocity, fps, through net free flow area in tube banks to prevent flue-dust erosion

Type of Firing or Fuel	Multi-pass	Single pass
Pulverized coal	75	75*
Spreader stoker	50	60
Chain-grate stoker, anthracite	60	75
Chain-grate stoker, coke breeze	60	75
Chain-grate stoker, bituminous	100	100
Underfeed stoker	75	100
Blast-furnace gas	75	100
Cyclone Furnace	—	100
Wood or other waste fuels containing:		
Sand	50	60
Cement dust	—	45
Bagasse	60	75

*For PC units burning fuels having more than 30% ash on a dry basis, limit the maximum velocity through the free flow area to 65 fps. For PC units burning coals producing fly ash with known high abrasive tendencies, such as Korean or Central Indian coals, limit the maximum velocity through free flow area to 45 fps.

Erosion may also be a problem in slag- and ash-handling equipment. If the unit is of the slag-tap variety, the molten refuse or slag tapped from the furnace must be cooled to be conveniently handled. This is done with water and the quenched product is usually small particles, like coarse sand, which, regardless of the mode of transport, tend to wear the surfaces of the conveying system. When water is used for transport, the pump, pipe lining, and turns in pipes or sluices are especially subject to localized wear and are usually protected by replaceable linings of alloy steel or chilled cast iron.

Design and operation of slag-tap units

The method of disposal of coal ash by tapping from a boiler furnace was evolved in 1926, more by accident than by design, in a boiler furnace originally expected to operate under dry-ash disposal conditions. During operation, the low-fusion ash melted, collected in a pool at the bottom of the furnace, and was drained at intervals by means of an improvised arrangement.

Many features of this furnace, the forerunner of later slag-tap furnaces, were totally inadequate for the for-

mation, retention and disposal of fluid ash. The furnace bottom was of ordinary brick that quickly disintegrated under the chemical action of the molten slag. It was also apparent that the proper handling of a stream of molten slag was a difficult undertaking. Nevertheless, this early experience opened the way to the development of a method for easier handling and disposal of refuse in furnace operations. Some of the important requirements for adequate slag-tap furnace design that evolved from this development are:

1. The slag in the furnace must be kept fluid. The furnace temperature must be high and the slag-tap furnace should be designed to withstand the maximum temperature reached during combustion, which is usually in excess of 3000F.

2. Since fluid slag is heavy as well as extremely hot, it must be securely contained in those regions of the furnace where it tends to collect.

3. The interior surface of the furnace must be chemically inactive to the constituents of the hot slag.

4. Means must be provided to drain slag from the furnace as fast as it is formed, or at least at frequent intervals.

5. Once the molten slag has left the furnace, it must be cooled to a temperature that renders it suitable for ultimate disposal.
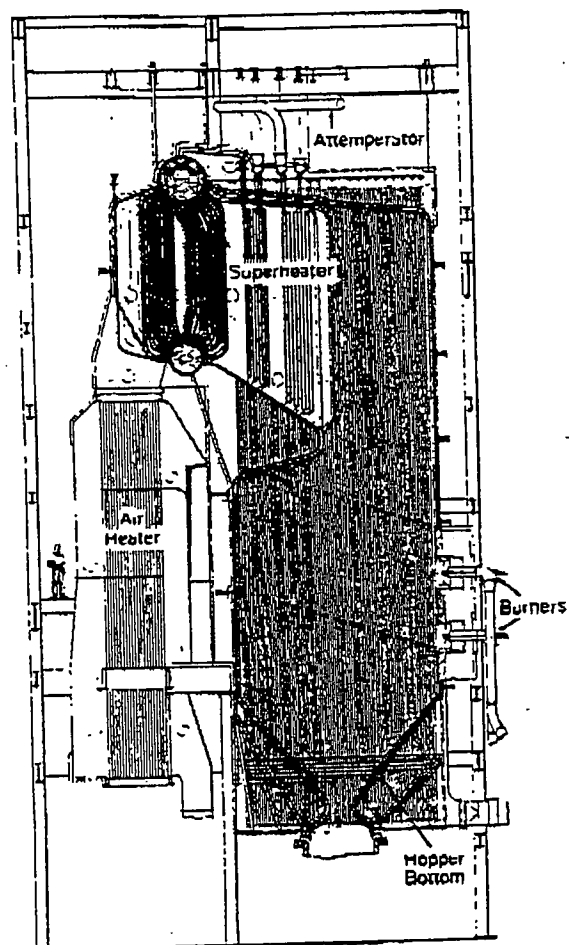

Fig. 11 Boiler with dry-ash furnace designed for horizontal gas flow through tube banks without baffles.

To withstand the high temperatures noted above, all sides and the floor of the furnace are water cooled. More or less unsuccessful attempts were made at different times to employ other arrangements, including solid refractories in brick and molded form, air-cooled refractories, and water-cooled tubes on various centers embedded in a variety of refractories.

The continuous-tap arrangement for withdrawing molten slag from the furnace is illustrated in Fig. 12. The molten slag disintegrates as it comes in contact with water in the slag tank, and this final slag product is conveyed to disposal.

The difficulty in tapping slag of high fluid temperature is most evident during low-load operation. Under these conditions, even a coal with a slag of medium fluid temperature may not be suitable for slag-tapping, since the furnace temperature may not be sufficiently high to attain the degree of fluidity necessary for tapping.

One of the most important attributes of the slag-tap furnace is the coating of sticky ash that covers a portion of the furnace walls near the bottom. The sticky surface of molten ash, deliberately maintained in selected high temperature zones, serves to entrain other transient particles. The ash so collected drains continuously toward the furnace bottom and is removed through the tap holes. The consequent reduction in the quantity of dust and ash leaving the boiler unit has a definite practical value, since it decreases the amount of dust to be handled by collectors and therefore decreases the size and cost of the dust collecting equipment.

It may be possible to reduce building costs in housing units with slag-tap furnaces, since they are usually built with flat floors, thus requiring less building height. In planning new buildings, this may be a significant factor in total first cost. Even in outdoor installations the height of the supporting steel structure can be reduced. Also, slag-tap units may be installed in older plants where it would be difficult, because of the greater height required, to install a unit designed for dry ash removal.
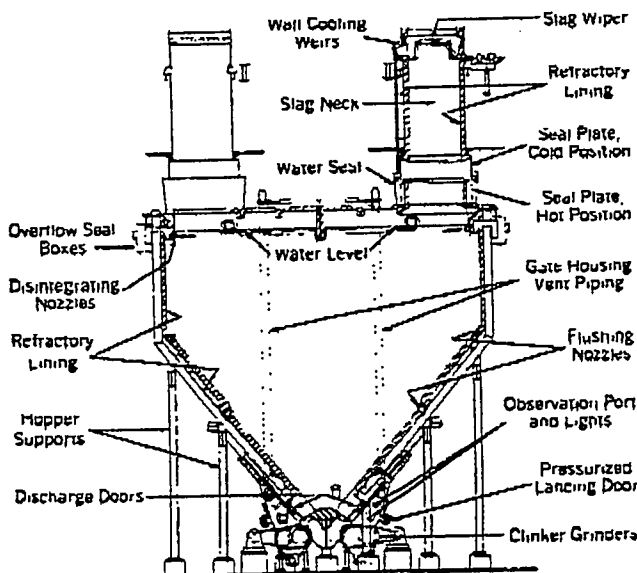

Fig. 12 Slag tank for a large utility unit for collecting low-viscosity molten ash when burning a midwestern coal. (Courtesy Allen-Sherman-Hoff Company.)
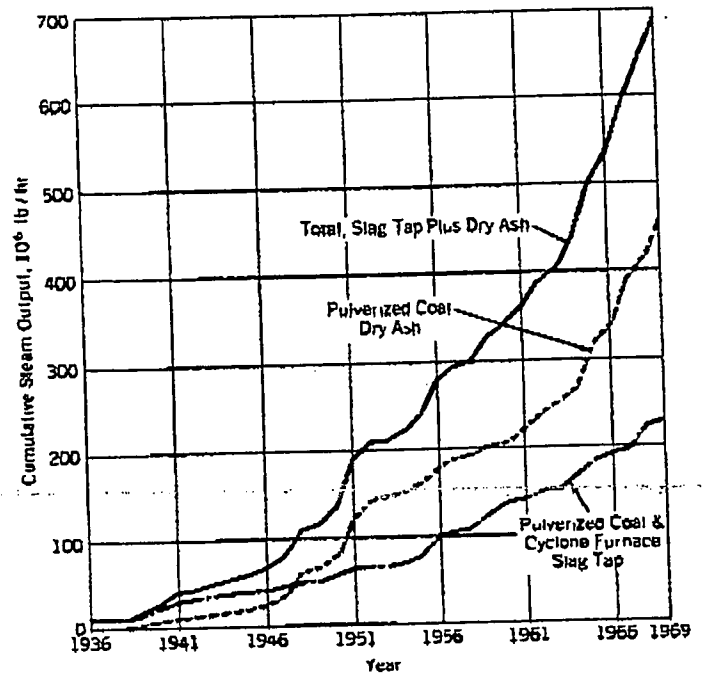

Fig. 13 Steam capacity of B&W slag-tap and dry-ash boiler units of 300,000 lb/hr and above, for a 34-yr period.

Dry-ash and slag-tap furnace installations

For the 34-year period 1936 through 1969, B&W sold 567 slag-tap and dry-ash boiler units in sizes of 300,000 lb of steam per hr and above, for a total capacity of over 683,000,000 lb of steam per hr. Of these, 208 units for 228,000,000 lb/hr, or 33% of the total, were of the slag-tap type, and 359 units for 455,000,000 lb of steam per hr were of the dry-ash type. In the size range considered, the steam output of B&W dry-ash and slag-tap units by years is shown graphically in Fig. 13. In the earlier years of the period, the greater part of the steam output was produced with slag-tap units. In the middle years of the period, the proportion of dry-ash units steadily increased, and in 1948 virtually an equal amount of steam was produced by each type. In the years 1948 through 1969 more steam was produced by dry-ash units than by the slag-tap type.

The statistics plotted in Fig. 13 for the units included in the study, indicate a steep increase in the application of the dry-ash method of burning pulverized coal after the early period. One important reason for this increase is the fact that boiler designers, by improvements in burners, furnace proportions, and the arrangement of heating surfaces to preclude slagging and fouling, largely overcame the earlier difficulty of keeping the dry-ash unit free of slag or troublesome ash.

Ash and slag removal from heating surfaces

Furnace walls and convection-pass surfaces can be cleaned of ash and slag while in operation by the use of sootblowers using steam or air as a blowing medium. Tubular air heaters having tubes 20 feet long or less can be cleaned by air or steam blowers. With tubes over 20 feet long, cleaning is done by circulating metal shot through the tubes for ash removal.

Coal-ash deposition

Ash deposition in various boiler zones is an important factor to be considered by the boiler designer and operator. Initially, ash deposits on furnace walls act as insulation, thereby delaying cooling of flue gases. This can cause an increase in steam temperature and is one factor that can cause the deposits to advance into normally cooler parts of the boiler. If the deposits are not removed during operation, accumulations forming on furnace walls may cause excessive gas temperatures downstream, or in some cases, these accumulations may fall and damage pressure components. Accumulations in tube banks may block gas passes and require a boiler outage for manual cleaning.

The occurrence and severity of ash deposition depend largely on the coal-ash composition and amount of coal ash, but can be strongly influenced by the method of firing, design of equipment, and the operating conditions. Some of the influencing conditions are shown in Table 5. In practice, the design parameters and operating conditions are determined by the characteristics of the ash. For example, if the ash does not tend to form troublesome deposits, the furnace wall surfaces will require few, if any, sootblowers for cleaning. The boiler can be designed with deep banks of closely spaced superheater or reheater tubes located in high-gas-temperature zones. Relatively few sootblowers will be required and these can be operated at high speeds, with small nozzles and low pressures.

On the other hand, if the ash produces hard, massive deposits, the superheater and reheater tube banks are designed to permit ease of deposit removal. For instance, lateral tube spacing is increased, tube bank depth is decreased, and the banks are located in cooler-gas-temperature zones. Additional sootblowers, operating at maximum capability, may be required.

It is therefore essential to identify the factors responsible for the fouling characteristics of various coals, so that the optimum design can be achieved with the coal or coals being burned. This has required a large amount of research into the nature of coal and coal ash, the extent and nature of ash deposits, the relationship between coal-ash composition and ash deposition, and the effect of boiler operating variables. The results of some of this research were discussed earlier in the chapter when it was noted that coal ash was derived from mineral matter associated with the coal-forming plants and from inorganic constituents added to the coal deposit from outside sources during or following coal formation. These materials are usually referred to as inherent and adventitious mineral matter, respectively. They occur in many forms, including shales, kaolins, sulfides, carbonates, chlorides and others. Identification of the mineral species is difficult for a variety of reasons. However, the presence of several of them has long been associated with severe ash deposition, fouling, and corrosion, after the organic material is burned and the inorganic constituents are carried through the boiler by the flue gases.

An obvious answer to the problem is to remove all of the coal ash. Although some ash removal is possible and actually accomplished commercially, the task is very difficult, and economic and technical limits are encountered. Therefore, it is imperative to acquire a comprehensive understanding of the nature of coal ash and its behavior during and following the combustion process. This is being accomplished through laboratory, pilot-plant, and field investigations being carried out in the U.S. and abroad.

The results of some of these investigations are given in the following section which briefly reviews some of the ash-deposit types and their effect on boiler operation, outlines some of the factors affecting ash deposition, and describes techniques used to assess deposit severity.

Ash-deposit types

A portion of the coal ash and its combustion products is carried by the flue gases through the boiler, regardless of the method of coal firing. Much of the ash passes through the boiler without depositing or, in the case of the slag-tap furnace, is removed as molten slag. The ash passing through the boiler is subject to various chemical reactions and physical forces which lead to deposition on stationary surfaces. Flue-gas, particle and surface temperatures, gas velocity, flow patterns, as well as other factors such as particle size and composition, influence the amount and nature of ash depositing on cooled surfaces. Deposits are frequently divided into three broad types:

1. Fused slag deposits forming on furnace walls and other surfaces exposed to predominantly radiant heat transfer.

2. High-temperature bonded deposits occurring on convection heating surfaces, especially superheaters and reheaters.

3. Low-temperature deposits occurring on air heaters and economizers.

Fused slag deposits

Slag deposits are usually associated with physical transport of molten or tacky particles by the flue gases. Condensation of species vaporized by the flame also can occur as the gases cool, causing enrichment of certain elements in the wall-slag deposits. For slag-tap furnaces, a portion of the furnace is usually designed to provide a continuous layer of slag near or in the combustion zone. Beyond the slagging zone, and in dry-ash pulverized coal boilers, accumulation of deposits can cause the problems described earlier. Fig. 14 shows an example of severe slagging encountered on one boiler. Deposits forming beyond the slagging zone are normally removed with short retractable sootblowers. Removal of some slags can be very difficult, depending on several factors that are discussed later.

High-temperature bonded deposits

The formation of deposits on convection heating surfaces has been the subject of a great deal of research. The extent of these deposits varies greatly from coal to coal and with changes in the furnace wall condition. They can be very troublesome because they can obstruct gas passages, and are sometimes very difficult to remove with normal in-service cleaning equipment.

Investigators have identified several types of bonded deposits, including alkali, calcium, phosphorus, and silica

Table 5
Design parameters—coal and coal ash

Fuel characteristics

1. Properties of coal substance

a. Physical, including density, hardness, specific heat, thermal expansion and thermal conductivity.

b. Chemical—behavior during heating, i.e., carbonization, gasification, and combustion.

Technological properties

1. Proximate analysis
2. Ultimate analysis
3. Free-swelling index
4. Differential thermal analysis
5. Thermogravimetric analysis
6. Effluent gas analysis
7. Grindability
8. Calorific value
9. Sieve analysis
10. Ignitability
11. Abrasiveness

2. Properties of coal ash

Determined by the concentration and type of minerals in the coal containing the following elements.

a. Alkalis   e. Calcium-Magnesium
b. Sulfur   f. Iron
c. Chlorine   g. Silica
d. Phosphorus   h. Alumina

Technological properties

1. Fusion temperatures
2. Viscosity of slag
3. Surface tension of slag
4. Volatility of constituents in slag
5. Sintering temperature and strength of ash

Boiler design and operation

1. Firing method
a. Slag tap, PC and cyclone
b. Dry ash, PC
c. Fuel bed, chain-grate, and spreader stoker

2. Furnace design
a. Rating
b. Wall construction
c. Type, number and arrangement of burners
d. Furnace geometry
e. Exit-gas temperature

3. Tube bank design
a. Horizontal or vertical tubes
b. Spacing, side and back
c. Depth of bank
d. Alignment
e. Freedom of tube movement

4. Combustion conditions
a. Excess air
b. Air temperature
c. Load cycles
d. Residence time

5. Properties of flue gases
a. Temperature
b. Flow patterns
c. Composition

6. Properties of entrained ash
a. Dust loading
b. Size consist
c. Composition
d. Microstructure

Sootblower design and operation

1. Blowing medium
a. Air or steam
b. Pressure
c. Temperature

2. Type of sootblower
a. Short retractable
b. Long retractable
c. Fixed position rotating
d. Traveling frame

3. Location and spacing of sootblowers

4. Sootblower nozzles
a. Type
b. Size
c. Number
d. Angle of attack

5. Lance-tube speed
a. Rotational
b. Axial

6. Frequency of blower operation

Fig. 14 Furnace-wall slag deposits.

Table 6
Analysis of superheater deposits vs fly ash from a boiler firing an Illinois coal

Constituents of Ash, % by Wt	Fly Ash	Superheater Deposits	
		Outer Layer	Inner Layer
SiO_2	37.4	36.2	15.8
Al_2O_3	15.3	12.9	9.0
Fe_2O_3	20.8	19.9	11.8
TiO_2	1.0	1.1	0.5
CaO	5.2	9.1	3.9
MgO	0.9	1.0	0.8
Na_2O	3.8	4.3	5.9
K_2O	2.7	2.4	9.0
SO_3	3.6	13.1	43.3
Not Determined	3.3	0.0	0.0
Total	100.0	100.0	100.0
Water Solubility, %	—	12	60

the normal alkali equivalent, which is attributed to the formation of complex iron and aluminum sulfates. Investigations carried out by B&W indicate that this white inner layer is formed over a period of time as a reaction product of the gaseous sulfur oxides and fly ash depositing on tube surfaces. Inspections and analyses were made of deposits forming on an air-cooled probe in a boiler firing an Illinois coal. After one week of exposure to flue gases at approximately 2000F, the deposit formed on the metal surface, controlled at 1050F, consisted of loosely held fly ash with no evidence of a white bonding material. The white layer began forming after two weeks and its thickness progressively increased throughout the remainder of the 11-week test period.

The white layer not only provides a bond for the bulk fly-ash deposit, but can also be responsible for corrosion of high temperature tubes. This is discussed in a subsequent section in this chapter.

The nature and amount of bulk deposit forming on the tube are functions of fly-ash characteristics, which in turn are related to the coal-ash composition, firing method, and furnace operating conditions. For fly ash with similar properties, the rate of ash deposition is proportional to the amount of fly ash being transported by the flue gases.

types, depending on the bonding agent. They appear to be associated with vaporization of coal ash constituents during combustion and subsequent condensation on fly-ash particles on surfaces. The alkali and calcium-bonded deposits are more common in the United States, whereas problems with these and the other types have been described by investigators in other countries. The occurrence and severity of fouling by these bonded deposits depend chiefly on the composition of the coal ash, but are influenced by the method of firing, the design of equipment, and the conditions of operation.

Since the alkali-bonded deposits are generally acknowledged as the most prevalent, especially with U.S. bituminous coals, they will be treated more extensively in the following sections. An example of severe fouling on superheater tubes is shown in Fig. 15.

Deposits found in the superheater and reheater regions of the boiler are typically composed of a thin inner layer with a characteristic composition and appearance distinctive from the outer layer, which has a composition similar to the fly ash. Table 6 gives a comparison of the two deposit layers and the fly ash from a boiler firing an Illinois coal.

The inner layer is normally tightly attached to the tube surface and there is strong evidence that a liquid phase exists within the layer at operating temperatures. This layer provides a bond between the superheater tube and the outer layer of sintered fly ash which forms the bulk of the deposit and becomes massive under certain conditions.

It is apparent that the inner layer is rich in sodium and potassium, and it usually contains sulfate in excess of

Fig. 15 Ash deposits on secondary superheater tubes.

Low-temperature deposits

Formation of deposits in the low-temperature zones such as the economizer and air heater is usually associated with condensation of acid or water vapor on cooled surfaces. Other types of deposits, especially in the economizer of boilers with bed-type combustion systems, have also been reported while firing coals with relatively small amounts of phosphorus. Phosphatic deposits have been extremely hard, but the problem is restricted to a limited number of boilers, located mostly in Europe.

Condensation of acid or water vapor can be encountered when metal surfaces are allowed to cool below the acid or water dew points. The sulfuric acid dew point depends on the amount of sulfur trioxide present in the flue gases, but it is usually between 250 and 300F for SO_3 concentrations of 15-30 parts per million. The water dew point depends on the coal and air moisture levels, the hydrogen in the coal, the excess air, and the amount of steam used in sootblowing. It is usually in the range of 105-115F for coal firing. On air heaters, where metal temperature is a function of both air and flue gas temperatures, condensation on low temperature surfaces of tubular heaters can occur on tubes near the air inlet and flue gas outlet or on cold-end baskets on regenerative heaters as they are being heated by the flue gases on each cycle. Several factors, such as maldistribution of air or flue gases, excessively low exit-gas temperatures and very low air temperatures can aggravate the problem of condensation. Low gas flow during low load, start-up and other similar periods can also result in condensation of water and acid.

The deposits themselves can be composed of three types of material. First, the acid attack can produce various amounts of corrosion product next to the metal depending on the amount of acid available, the temperature, and the type of metal. Second, this wet deposit can trap fly ash which adds to the bulk of the deposit. Third, the acid can react with constituents such as iron, sodium and calcium in the fly ash to form sulfates, which increase the deposit bulk.

The deposits are usually characterized by low pH (highly acidic); many contain hydrated salts, and for most bituminous coals they are water soluble. In this case, deposits can sometimes be water washed from low-temperature surfaces. However, in some cases when the coal ash contains large amounts of materials such as calcium, the reaction product $CaSO_4$ is nearly insoluble. The deposits that form are very hard and difficult to remove by washing. Complete plugging of gas passes also makes removal by water washing more difficult, even when the deposits are water soluble.

Deposition can be eliminated by operating the metal temperatures well above the acid dew point temperature of the flue gas, but this would result in a significant loss in boiler efficiency. Improvements in design to get more uniform air and gas distribution, better materials of construction and improved cleaning systems have been combined to minimize the low-temperature deposit problem while operating at relatively low exit-gas temperatures.

Evaluation techniques

The development of laboratory techniques for evaluating the slagging and fouling tendencies of coals is an important and necessary step in providing optimum boiler designs for each fuel type. Typical ASTM tests are usually inadequate to distinguish fouling tendencies of various coals. Extremes in ash fusion temperatures may be indicative of differences in fouling and slagging potential, but most coal ash falls within a narrower range and the fusion temperatures are therefore inadequate. Operating experience from commercial boilers is essential in establishing the actual behavior of coals, but controlled testing of large boilers is unwieldy and expensive. Furthermore, it is impossible in these large boilers to examine very small coal samples, such as core drillings from a new mine. Thus, information that would be of value in establishing boiler and cleaning equipment design parameters might be delayed, probably until a new mine is operating, and the boiler has already been designed. It is therefore essential that laboratory tests be available to evaluate the behavior of coals. Several methods have been developed by B&W to aid in providing optimum design parameters for various coal-ash types.

Wall slagging

The deposit forming on water-cooled furnace walls usually varies in appearance, depending on the composition, atmosphere, and slag temperature. Adjacent to the tube surface, it is frequently porous and relatively loosely adherent to the tube surface. As the deposit builds in thickness, the surface exposed to the flue gases becomes plastic, then fluid, if temperatures are high enough when it reaches an equilibrium thickness. However, the plastic slag is more difficult to remove as sootblowers can be almost ineffective in penetrating the viscous plastic shell that sometimes forms at the outside surface of the wall slag.

Various methods have been used in attempting to predict the slagging tendencies of a coal ash. Ash fusion temperatures, in some cases, provide an indication of the potential problems that might be encountered with a particular coal. For example, coal ash with extremely high fusion temperatures remains dry and little or no deposit forms on furnace walls. However, for coals with lower ash fusion temperatures, other factors are important. Coal-ash composition has also been shown to influence the slagging behavior of coal ash and formulas have been proposed to calculate softening temperature from ash composition, but here too, no correlation has been developed to enable prediction of wall-slagging tendency.

Extensive field tests, during which time-lapse movies and other observations were made, confirmed that the slags that were plastic were very difficult to remove. Viscosity measurements, usually made to determine flow characteristics for slag-tap performance, were extended to higher viscosity levels. These measurements showed that the slags most difficult to remove were plastic over a broad temperature range, whereas slags that were easy to remove were plastic over a relatively narrow temperature range (see Fig. 16). This relationship was observed for a number of coal-ash slags and efforts are
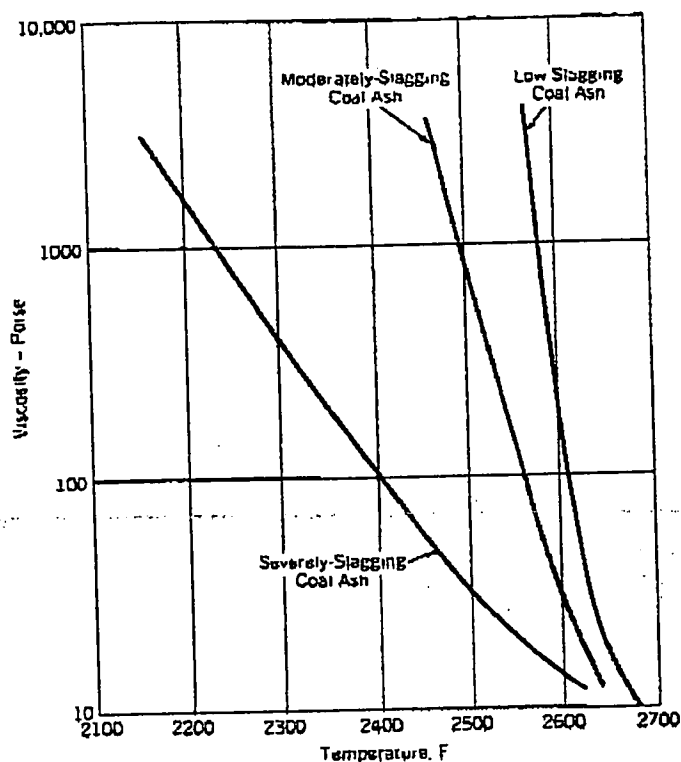
Fig. 16 Viscosity of wall slags (oxidizing atmosphere).

now being made to develop a correlation giving coal-ash viscosity in the plastic region as a function of temperature and slag composition, including relative amounts of FeO and Fe_2O_3. The influence of the iron oxidation state is very strong and the change in oxidation level may be due to changes in excess air. Fig. 17 shows the effect on viscosity by changing from an oxidizing to a reducing atmosphere over the slag melt. Flame impingement on furnace water walls can be responsible for creating a strongly reducing condition of the slag and causing severe wall slagging.
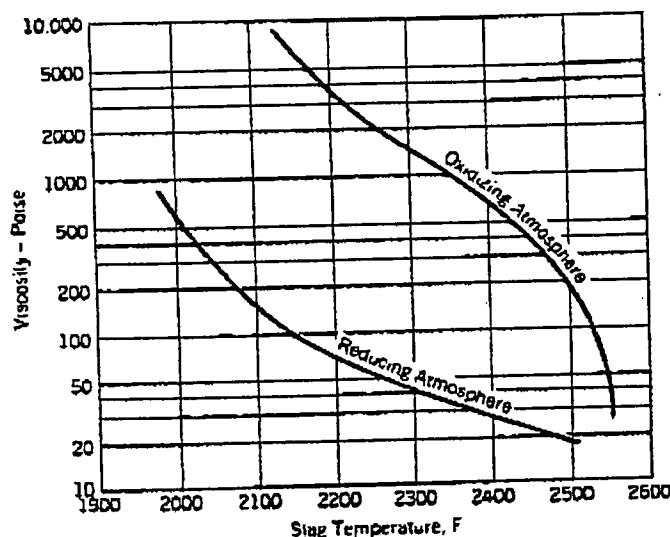

Fig. 17 Viscosity-temperature relationship.

High-temperature bonded deposits

Early research effort in this area was directed toward alleviating ash deposition by modifying boiler design, injecting additives, and improving boiler cleaning equipment. During this time, numerous coal analyses were obtained in an effort to isolate troublesome coal constituents, and concurrently to develop laboratory techniques for assessing the deposit-forming tendency of a coal. One technique, developed some time ago, has proved to be very useful and is still in use today. This technique, called the sintering test, determines the relative strength of a deposit. In this test, the fly-ash samples collected from the flue gases are passed through a 60-mesh U S. Standard screen to remove particles of slag and are then ignited to constant weight at 900F to remove any carbon that might be present. The ignited fly ash is then reduced to a minus 100-mesh size, and at least 24 cylindrical specimens (0.6-in. diameter by 0.75-in. long) are formed in a hand press at a pressure of 150 psi. At least six specimens are heated in air, usually at each of four temperature levels (1500, 1600, 1700 and 1800F) for 15 hours.

After the specimens have cooled slowly in the furnace, they are removed, measured, and then crushed in a standard metallurgical testing machine. The sintered or compression strength is then computed from the applied force and the cross-sectional area of the sintered specimen. The average strength of six specimens is used as the strength of the sintered fly ash at a particular sintering temperature.
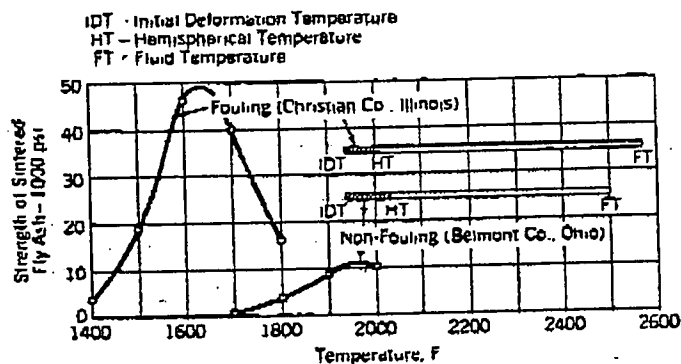

Fig. 18 A comparison of sintered strengths and ash fusion temperatures for a fouling and a non-fouling coal.

Extensive application of this method, combined with observation of operating boilers, showed that coals with a tendency to form troublesome deposits produced fly ash with high sintered strength. Conversely, low-strength fly ash was associated with non-fouling coals. The two extremes are illustrated in Fig. 18 which shows the strength of sintered fly ash for two coals having similar ash fusibility but widely varying fouling characteristics. This figure shows that ash fusion temperatures bear little relation to the tendency to form bonded deposits.

Coal samples were also obtained while the sintering information was being compiled. A relationship between total alkali content (Na_2O and K_2O, expressed as equivalent total Na_2O) and fly-ash sintered strength was observed for the samples collected. This trend is shown in
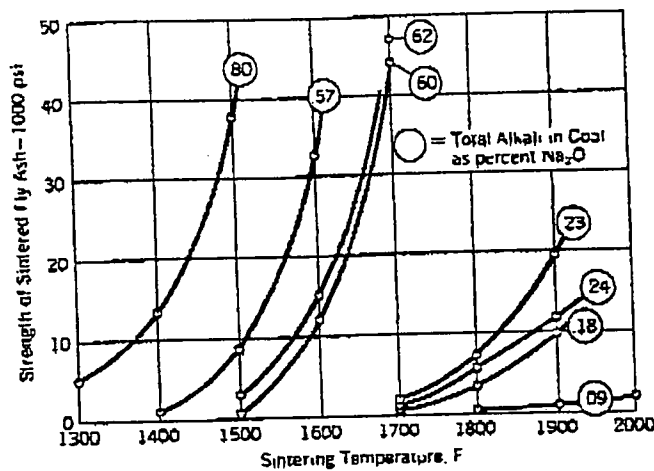
Fig. 19 Effect of alkali content in coal.

Fig. 19, which illustrates the higher coal-alkali content associated with high-strength fly ash. As knowledge of the factors affecting ash deposition increased, guidelines were established to arrive at suitable equipment designs for various fuels. The first such guideline, called a "fouling index," used total alkali content in the coal as a criterion. This index divided coal into three categories, based on the alkali content. Coals with 0.4% alkali or lower produced deposits that could easily be removed by sootblowers, but superheater fouling increased markedly when the alkali content of the dry coal was more than 0.6%. Between these two levels, intermediate fouling was encountered.

During this period, it was also learned that additives such as dolomite and magnesia have a pronounced effect on the strength of fly ash. For bituminous coals, which normally contain more acidic than basic constituents, magnesia was the most effective additive tested. Fig. 20 shows the effect of several additives. Subsequent field tests in which magnesia and high-magnesium dolomite were injected into boilers, confirmed that these additives could substantially lower sintered strength and reduce fouling with bituminous coals.

Development of laboratory tests

The fouling guidelines were improved as information was acquired from operating experience, sintering data, and coal analyses. However, the acquisition of data for improving guidelines was slow and expensive because it was dependent on field tests. This, of course, meant full-scale boiler tests under constant conditions with a large, consistent coal supply which became more difficult as unit size increased. In an effort to improve the efficiency and accuracy of obtaining data, a research program was initiated to develop a technique to evaluate the fouling potential of a coal based on information developed in the laboratory. The primary requirement for this step was the production of suitable fly ash for evaluation by the sintering test. This was accomplished by building a small coal-fired pilot plant.

Tests made in the pilot plant confirmed field experience, indicating that it could be used as a tool for evaluating ash-fouling tendency. Fig. 21 shows that fly ash from this pilot plant had widely differing strengths; those strengths related well with fouling history.

Numerous tests have been made with a variety of domestic and foreign coals. These coals were selected to provide a wide range of analyses and fouling potential when this information was known. The actual ranges of concentrations of coal-ash constituents for all coals and for the bituminous coals tested in this and other programs are compared in Table 7 with the ranges typical of U.S. coals:

Table 7
Coal-ash constituents of pilot plant coals vs typical U.S. coals
Percent by weight

	All Coals Tested	Bituminous Coals Tested	Typical U.S. Coals
SiO_2	3.3–61	37 –61	20 –60
Al_2O_3	<5 0–43	13 –43	10 –35
Fe_2O_3	2 6–30	2 6–30	5 –35
TiO_2	0.3– 1.4	0.7– 1.4	0.5– 2.5
CaO	0.9–33	0.9– 9 2	1 –20
MgO	0.4–10+	0 4– 2.4	0.3– 4
Na_2O	0.1–14	0.1– 2.4	1 – 4
K_2O	0.2– 3.0	0.3– 3.5	0.1–12
SO_3	1 –23	—	

This comparison shows that information has been acquired for coals with constituent concentration ranges in some cases greater than those typical of U.S. coals, and thus indicates a very wide range of coal-ash compositions.

These experiments have demonstrated that sodium is the most important single factor affecting ash fouling. Potassium, which had been included in previous alkali-fouling indices, makes no perceptible contribution to sintered strength. The amount of water-soluble sodium, which is related to the more readily vaporized sodium, was shown to have a major effect on sintered strength.

This result was achieved by washing the coal with hot condensate in the laboratory to remove the water-soluble sodium which is related to the more readily vaporized
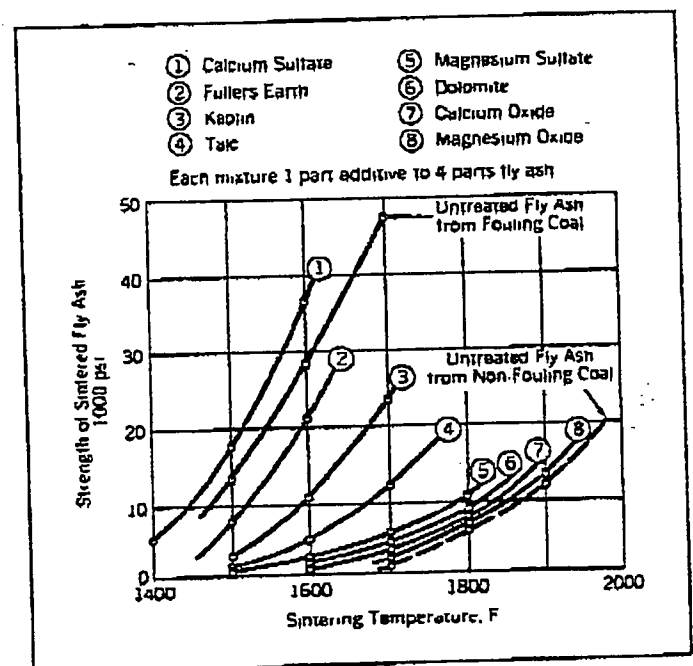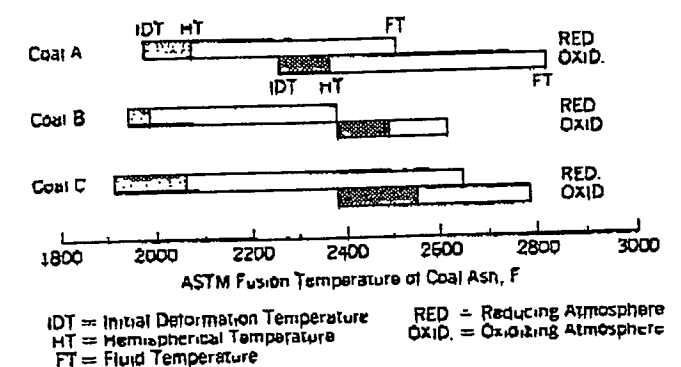

Fig. 20 Effect of additives.

IDT = Initial Deformation Temperature
HT = Hemispherical Temperature
FT = Fluid Temperature

RED = Reducing Atmosphere
OXID. = Oxidizing Atmosphere

Fig. 21 Comparison of sintering characteristics of laboratory fly ash.

sodium. The washed coal was then fired in the pilot plant and sintered at various temperatures. In one case a fouling coal washed with hot condensate and sintered at 1700F had a fly-ash strength only 10% of the value obtained with an unwashed sample at the same sintering temperature.

Information from the tests carried out thus far is being processed to develop correlations between fly-ash sintered strength and coal-ash composition, using both total and water-soluble sodium.

Lignites

Tests with several North Dakota and Canadian lignites, and an Australian brown coal, all of which have ash with high alkali contents (CaO, MgO, Na_2O, K_2O), have shown that fly ash from these coals will sinter at low temperatures, but sintered strengths remain low regardless of fouling tendency. Since this ash contains large amounts of alkaline materials, which react with sulfur dioxide to form sulfates, the bond is probably a sulfate type.

Effect of operating variables

Although the predominant factors affecting ash deposition are the amount and composition of the coal ash,

boiler operating conditions have also been demonstrated to affect deposition. Some of the factors that have been studied are excess air, firing method, and deposit-time temperature, which is a function of the gas-tube temperature relationship as well as ash properties.

The effect of excess air variation on viscosity is indicated in Fig. 17. It was noted earlier that plastic slag is most difficult to remove from furnace walls, and this figure shows that variations in atmosphere from reducing to oxidizing have a major effect on the nature of the ash. In practical terms, this means that care must be exercised in maintaining proper coal/air ratios at all times. If imbalances are allowed to occur, the slagging may be aggravated. Flame impingement on furnace walls, or operating several burners with less than theoretical air required for combustion and others at high excess-air levels, are typical ways in which this can occur. Increased slagging can also raise temperatures entering the convection bank, which leads to higher gas and deposit temperatures, thereby increasing deposit strength (*see Fig. 19*). Thus, although excess air has no direct effect on deposit strength, the higher gas temperatures caused by increased furnace wall slagging do affect superheater deposition.

Since deposition appears to be associated with vaporization of coal ash constituents, this phenomenon has been studied extensively. Vaporization is strongly dependent on mineral-matter type and on time and combustion temperature. Combustion temperature in turn is affected by heat release rate (including firing method), excess air, combustion air temperature, and coal characteristics. The rate of deposition is proportional to the amount of ash suspended in the flue gases and actual operation can be more severe for the lower strength deposits because of the higher rate of deposition. For bituminous coals only a small amount, usually less than 5%, of the suspended ash is deposited on convection banks, but for lignites this figure may be much greater.

Sintering time or reaction time is also a very important factor in determining deposit characteristics. Fig. 22 shows that, if a deposit is not removed promptly, the strength of the deposit increases many times. Thus, es-
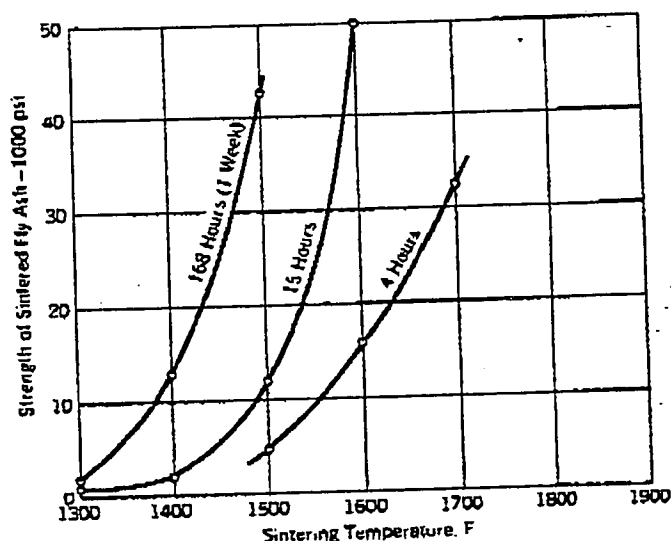

Fig. 22 Effect of sintering time.

tablishing sootblower operating frequency and coverage is also an extremely important facet of the overall problem of ash deposition.

Coal-ash corrosion

Serious external wastage or corrosion of high-temperature superheater and reheater tubes was first encountered in coal-fired boilers in 1955. Tube failures resulting from excessive thinning of the tube walls, as shown in Fig. 23, occurred almost simultaneously in the reheater of a dry-ash furnace boiler and the secondary superheater of a slag-tap furnace unit. Corrosion was confined to the outlet tube sections of the reheater and the secondary superheater, which were made from chrome-ferritic and stainless steel alloys, respectively.

Significantly, these boilers were among the first to be designed for 1050F main and reheat steam temperatures; also, both units burned high-sulfur, high-alkali coals from central and southern Illinois, which were causing chronic ash-fouling problems at the time.

Early investigations showed that corrosion was found on tube surfaces beneath bulky layers of ash and slag. When dry, the complex sulfates were relatively innocuous, but when semi-molten (1100-1350F), they corroded most of the alloy steels that might be used in superheater construction, as well as other normally corrosion-resistant materials.

At first, it appeared that coal-ash corrosion might be confined to boilers burning high-alkali coals, but complex sulfate corrosion was soon found on superheaters and reheaters of several boilers burning low-to-medium alkali coals. Where there was no corrosion, the complex sulfates were either absent or the tube-metal tempera-
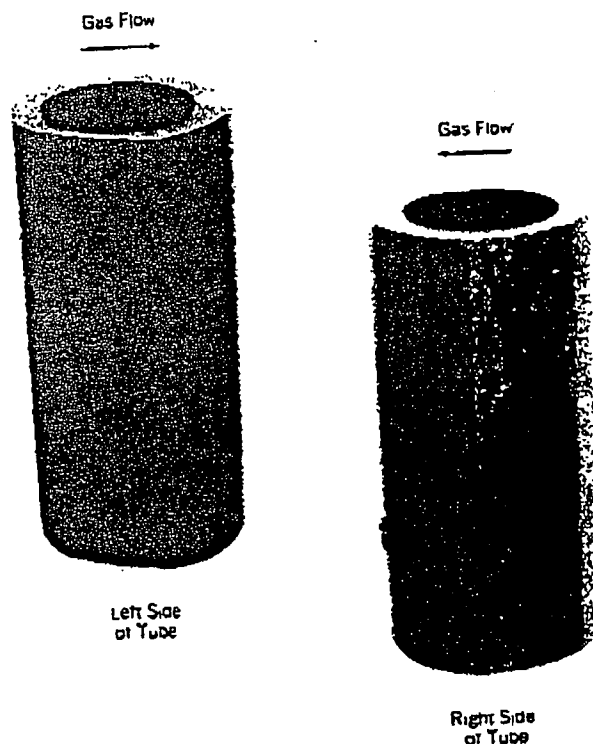
tures were moderate (less than 1100F). The general conclusions drawn from this survey of corrosion were:

1. All bituminous coals contain enough sulfur and alkali metals to produce corrosive ash deposits on superheaters and reheaters, and those containing more than 3.5% sulfur and 0.25% chlorine may be particularly troublesome.

2. Deposit temperature adjacent to the tube surface is the dominant factor affecting rate of corrosion. Experience has shown that the combination of tube-metal temperature and gas temperature provides a practical criterion for estimating deposit temperature and for establishing design temperature limits. Fig. 24, which is used as a guide in design, indicates stable and corrosive zones of fuel-ash corrosion as a function of gas and metal temperatures.
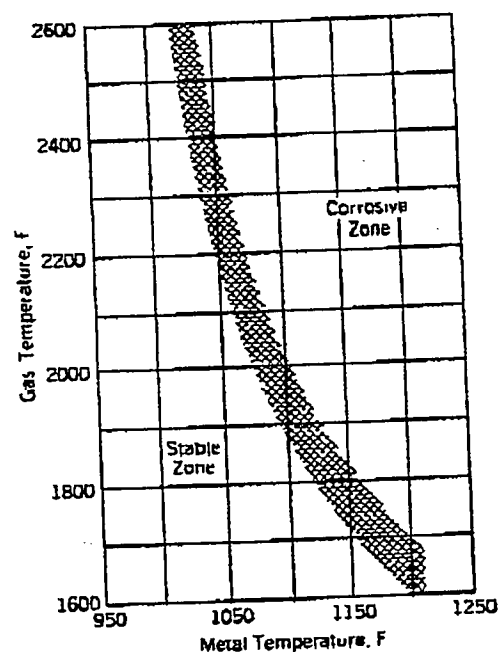

Fig. 24 Fuel-ash corrosion—stable and corrosive zones.

Based on this information, B&W modified the design of its boilers to reduce greatly the corrosion of superheaters and reheaters. These modifications included changes in furnace geometry, burner configuration, superheater arrangement, and the use of gas tempering, all of which reduced metal and gas temperatures and reduced temperature unbalances. Experience from these installations has shown that it is possible to operate boilers with main and reheat steam temperatures up to 1050F with little, if any, corrosion.

Meanwhile, there was a gradual return to the 1000F steam conditions for new plants, due primarily to economic factors and secondarily to coal-ash corrosion. This temperature level permits the use of lower-cost alloys in the boiler, steam piping, and turbine with substantial savings in investment costs, and it also provides a greater margin of safety to avoid corrosion. Steam temperatures will therefore probably remain on the current 1000F plateau until economics dictates the use of high-
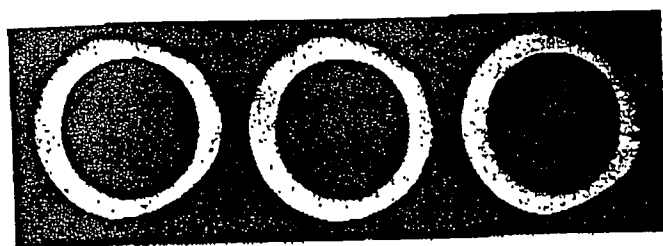

Fig. 23 Typical corroded 18Cr-8Ni tube from secondary superheater.

Steam / Fuel-ash effects on boiler design or operation

— Direction of Gas Flow

Fig. 25 Transverse sections of corroded tubes from secondary superheater platens.

temperature alloys and until methods are developed for avoiding corrosion at higher steam temperatures.

General characteristics of corrosion

External corrosion of superheaters and reheaters is concentrated on the upstream side of the tube, as shown in Fig. 25. The greatest metal loss usually occurs on the 10 and 2 o'clock sectors of the tubes and it tapers off to little or none on the back side of the tubes. The corroded surface of the tube is highly sculptured by a shallow macropitting type of attack. The amount of corrosion, as measured by reduction in tube wall thickness, varies considerably along the length of the tube, depending on local conditions, i.e., the position of the tube in the bank or platen, the proximity of sootblowers, the composition of ash deposits and, most importantly, the gas and metal temperatures.

The corrosion rate is a nonlinear function of metal temperature (Fig. 26). The corrosion of both chrome-ferritic and 18Cr-8Ni stainless steels increases sharply above a temperature of 1150F, passes through a broad maximum between 1250 and 1350F, and then decreases rapidly at still higher temperatures.

The highest corrosion rates are generally found on the outlet tubes of radiant superheater or reheater platens opposite retractable sootblowers. Values ranging from 50 to 250 mils/year have been observed on 18Cr-8Ni stainless steel tubes under these adverse conditions.
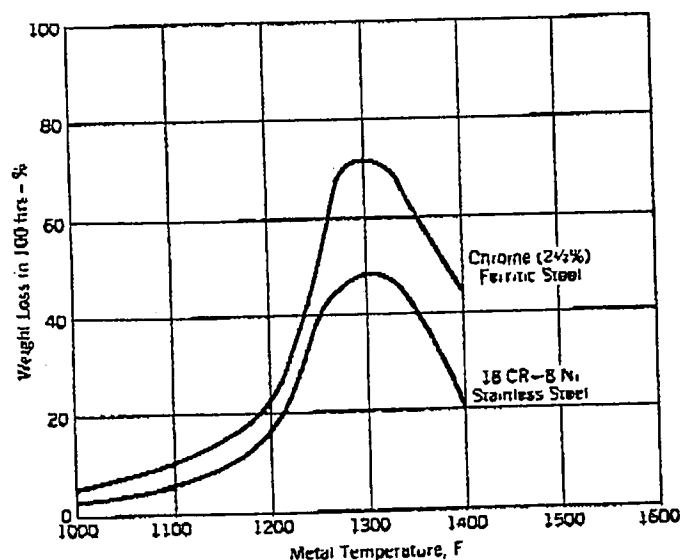
When similar high-temperature surfaces (1100-1175F) are arranged in convection tube banks so they are shielded from direct furnace radiation and sootblower action, corrosion rates are much lower, ranging between 5 and 20 mils/year.

Corrosive ash deposits

Corrosion is rarely found on superheater or reheater tubes having only dusty deposits. It is nearly always associated with sintered or slag-type deposits that are strongly bonded to the tubes. Such deposits consist of at least three distinct layers. The outer layer, shown diagramatically in Fig 27, constitutes the bulk of the deposit and has an elemental composition similar to that of fly ash. Though often hard and brittle, this layer is a porous structure through which gases may diffuse. Innocuous by itself, it plays an important part in the formation of an intermediate layer that contains the corrosive agents

The intermediate layer, frequently called the white layer, is a white-to-yellow colored material which varies in thickness from $\frac{1}{32}$ to $\frac{1}{4}$ in. It usually has a chalky texture where corrosion is mild or nonexistent but is fused and semi-glossy where corrosion is severe. In the latter condition this layer is difficult to remove as it is so firmly bonded to the corroded surface beneath.

Upon heating in air, the intermediate layer melts around 1000F and slowly discolors and hardens into a hard mass resembling rust. Chemical analyses of this layer show that it contains higher concentrations of potassium, sodium and sulfur than does the parent coal

Fig. 26 Effect of temperature on corrosion rate.

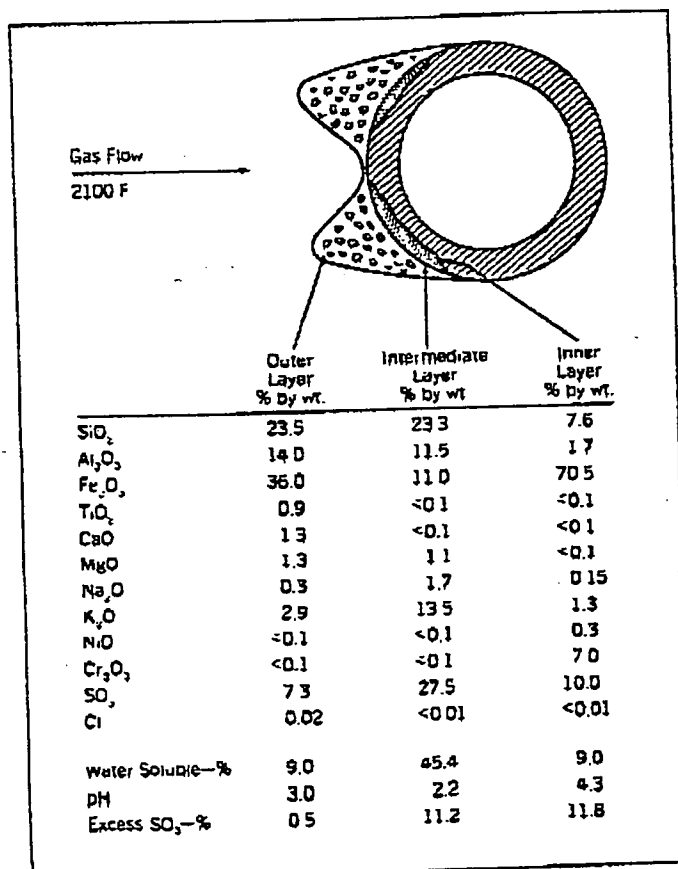|	Outer Layer % by wt.	Intermediate Layer % by wt	Inner Layer % by wt.
SiO$_2$	23.5	23.3	7.6
Al$_2$O$_3$	14.0	11.5	1.7
Fe$_2$O$_3$	36.0	11.0	70.5
TiO$_2$	0.9	<0.1	<0.1
CaO	1.3	<0.1	<0.1
MgO	1.3	1.1	<0.1
Na$_2$O	0.3	1.7	0.15
K$_2$O	2.9	13.5	1.3
NiO	<0.1	<0.1	0.3
Cr$_2$O$_3$	<0.1	<0.1	7.0
SO$_3$	7.3	27.5	10.0
Cl	0.02	<0.01	<0.01
Water Soluble—%	9.0	45.4	9.0
pH	3.0	2.2	4.3
Excess SO$_3$—%	0.5	11.2	11.8

Fig. 27 Analyses of typical ash deposit from 18Cr-8Ni superheater tube.

ash. A large part of this deposit is water soluble and the water-soluble fraction is always acidic. The identification of compounds making up the intermediate layer is difficult because its constituents are not well crystallized. The normal sulfates are conspicuously absent and the complex alkali sulfates are detected irregularly. The most common compounds found are $Na_3Fe(SO_4)_3$ and $KAl(SO_4)_2$ although other complex sulfates are thought to be present.

Laboratory studies have shown that complex alkali sulfates, when molten, rapidly corrode most, if not all, superheater alloys. Corrosion begins between 1000 and 1150F, depending on the relative amounts of complex sodium and potassium sulfates present, and whether these are predominantly iron or aluminum-base compounds. Corrosion usually begins at the lower temperature where the sodium-iron-sulfate system is the major part of the intermediate layer, but corrosion is more severe and persists into a higher temperature range when the potassium-aluminum-sulfate system is the dominant one.

If the intermediate layer is carefully removed, a black, glassy inner layer is revealed, which appears to have replaced the normally protective oxide on the tube. This layer is composed primarily of corrosion products, i.e., oxides, sulfides and sulfates of iron, and other alloying constituents in the tube metal. It seldom exceeds $\frac{1}{16}$ in. thickness on corroded 18Cr-8Ni stainless steel tubes, probably because of its strong tendency to spall off when the tube cools. The layer containing corrosion products from chrome-ferritic alloys often reaches $\frac{1}{8}$ in. thickness and exhibits little tendency to spall as the tube cools.
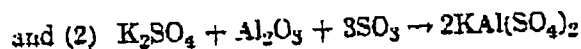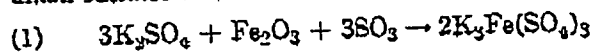
Corrosion mechanisms

The elements involved in coal-ash corrosion (sodium, potassium, aluminum, sulfur, and iron) are derived from the mineral matter in coal. The minerals supplying these elements include shales, clays and pyrite, which are commonly found in all coals.

During the combustion of coal, these minerals are exposed to high temperatures and strongly reducing effects of carbon for very short periods of time. Although comparatively stable, the mineral matter undergoes rapid decomposition under these conditions. Some of the alkalies are released or volatilized as relatively simple compounds, which have "dew points" in the 1000-1300F range. Furthermore, the pyrite is oxidized, releasing SO_2 with the formation of a small amount of SO_3, leaving a residue of iron oxide (Fe_2O_3).

By far the largest portion of the mineral matter or its derived species react to form the glassy particulates of fly ash. The fly ash and volatile species in the flue gases tend to deposit on the tube surfaces in a selective manner and subsequent reactions between these materials occur over long periods of time.

In the formation of corrosive deposits, fly ash first deposits on the superheater and reheater tubes. Slowly, over a period of weeks, the alkalies and the sulfur oxides diffuse through the layer of fly ash toward the tube surface. In the lower temperature zone of the ash deposit, chemical reactions between the alkalies, the sulfur oxides, and the iron and aluminum components

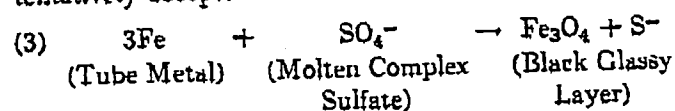of the fly ash result in the formation of the complex alkali sulfates as follows:

$$(1) \quad 3K_2SO_4 + Fe_2O_3 + 3SO_3 \rightarrow 2K_3Fe(SO_4)_3$$

$$and \ (2) \quad K_2SO_4 + Al_2O_3 + 3SO_3 \rightarrow 2KAl(SO_4)_2$$

Similar reactions occur with sodium sulfate (Na_2SO_4), although the complex sodium sulfates are less apt to form at high temperatures because of their lower stability.

Recent work at B&W's Research Center has shown that SO_3 concentrations in ash deposits must be very high (1000-1500 ppm), compared to the level in the flue gas (10-25 ppm) in order to form the complex alkali sulfates in the intermediate layer. Hence the bulk of the SO_3 must come from the catalytic oxidation of SO_2 in the outer layer of the deposit.

When the SO_3 produced in the outer deposit exceeds the partial pressure of SO_3 over the intermediate deposit, the complex sulfates form via reactions (1) and (2) above. When the opposite is true, the complex sulfates begin to decompose, according to the reverse of reactions (1) and (2), until a new equilibrium is reached. Since the formation of SO_3 is temperature dependent, the reversibility of these reactions is also temperature dependent. As shown in Fig. 26, the corrosion rate increases with temperature, passes through a maximum between 1250 and 1350F, and then falls to a comparatively low level at higher temperatures.

The destructive reactions between the complex alkali sulfates and the tube metal and its oxides have not been fully defined. A number of theories have been advanced to account for the composition of the corrosion products and the high rate of metal wastage. One that has been tentatively accepted is shown below:

$$(3) \quad \underset{\text{(Tube Metal)}}{3Fe} + \underset{\substack{\text{(Molten Complex} \\ \text{Sulfate)}}}{SO_4^-} \rightarrow \underset{\substack{\text{(Black Glassy} \\ \text{Layer)}}}{Fe_3O_4 + S^-}$$

The temperature range of this rapid liquid-phase attack is bracketed by (a) the melting temperature of the mixture of complex alkali sulfates present, and (b) their thermal-stability limits. The extreme width of this temperature band is approximately 400F, or corrosion due to the complex alkali sulfates may range from as low as 1000F to a maximum of 1400F, depending on the species present in the intermediate layer.

Corrective measures

Various methods of combatting corrosion of superheater and reheater tubes have been used or suggested, including the following:

1. The use of stainless steel shields to protect the most vulnerable tubes.

2. Coal selectivity and the grinding of coals to a finer size

3. Improve combustion conditions, i.e., provide fast ignition, good mixing, and proper excess air.

4. Injection of additives (mainly magnesium- and calcium-bearing minerals) into furnace gases or directly on the tubes through sootblowers

5. The use of more corrosion-resistant alloys and ceramic coatings on the most vulnerable superheater and reheater tubes.

Low temperature coal-ash corrosion is covered in Chapter 13.

Fuel-oil ash

The ash content of residual fuel oil seldom exceeds 0.2%, an exceedingly small amount compared to that in coal. Nevertheless, even this small quantity of ash is capable of causing severe problems of external deposits and corrosion in boilers. Of the many elements that may appear in oil-ash deposits, the most important are vanadium, sodium, and sulfur. Compounds of these elements are found in almost every deposit in boilers fired by residual fuel oil and often constitute the major portion of these deposits.

Origin of ash

As with coal, some of the ash-forming constituents in the crude oil had their origin in animal and vegetable matter from which the oil was derived. The remainder is extraneous material resulting from contact of the crude oil with rock structures and salt brines, or picked up during refining processes, storage and transportation.

In general, the ash content increases with increasing asphaltic constituents in which the sulfur acts largely as a bridge between aromatic rings. Elemental sulfur and hydrogen sulfide have been identified in crude oil, and simpler sulfur compounds are found in the distillates of crude oil including thio-esters, disulfides, thiophenes and mercaptans.

Vanadium, iron, sodium, nickel and calcium in fuel oil were probably derived from the rock strata but some elements such as vanadium, nickel, zinc and copper probably came from organic matter from which the petroleum was derived. Vanadium and nickel especially, are known to be present in organo-metallic compounds known as porphyrins which are characteristic of certain forms of animal life. Table 8 indicates the amounts of vanadium, nickel and sodium present in residual fuel oils from various crudes.

Table 8
Vanadium, nickel and sodium content of residual fuel oils
(parts per million by weight)

Source of Crude Oil	Vanadium	Nickel	Sodium
Africa			
1	55	5	22
2	1	5	—
Middle East			
3	7	—	1
4	173	51	—
5	47	10	8
United States			
6	13	—	350
7	6	2.5	120
8	11	—	84
Venezuela			
9	—	6	480
10	57	13	72
11	380	80	70
12	113	21	49
13	93	—	38

Crude oil as such is not normally used as a fuel but is further processed to yield a wide range of more valuable products. For example, in a modern U.S. refinery the average product yield, as a percentage of total throughput, is:

Gasoline	44.4
Lube oil fraction	16.4
Jet fuel	6.2
Kerosine	2.9
Distillates	22.5
Residual fuel	7.6

Virtually all metallic compounds and a large part of the sulfur compounds are concentrated in the distillation residue, as illustrated for sulfur in Table 9. Where low-sulfur residual fuel oils are required, they are obtained by blending with suitable stocks, including both heavy distillates and distillation from low-sulfur crudes. This procedure is also used occasionally if a residual fuel oil must meet specifications such as vanadium, or ash content.

Table 9
Sulfur content in fractions of Kuwait crude oil

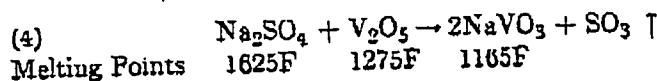| Fraction	Distillation Range, F	Total Sulfur % by Weight
Crude oil	—	2.55
Gasoline	124-253	0.05
Light naphtha	257-300	0.05
Heavy naphtha	307-387	0.11
Kerosine	405-460	0.45
Light gas oil	477-516	0.85
Heavy gas oil	538-583	1.15
Residual oil	588-928	3.70

Source, Article by F. E. Hixon, Shell Refining and Marketing Co., Ltd., *Chemistry and Industry*, March 26, 1955, page 333.

Release of ash during combustion

Residual fuel oil is preheated and atomized to provide enough reactive surface so that it will burn completely within the boiler furnace. The atomized fuel oil burns in two stages. In the first stage the volatile portion burns and leaves a porous coke residue, and in the second stage the coke residue burns. In general, the rate of combustion of the coke residue is inversely proportional to the square of its diameter, which in turn is related to the droplet diameter. Thus, small fuel droplets give rise to coke residues that burn very rapidly and the ash-forming constituents are exposed to the highest temperatures in the flame envelope. The ash-forming constituents in the larger coke residues from the larger fuel droplets are heated more slowly, partly in association with carbon. Release of the ash from these residues is determined by the rate of oxidation of the carbon.

During combustion, the organic vanadium compounds in the residual fuel oil thermally decompose and oxidize in the gas stream to V_2O_3, V_2O_4 and finally V_2O_5. Although complete oxidation may not occur and there may be some dissociation, a large part of the vanadium originally present in the oil exists as vapor phase V_2O_5 in the flue gas. The sodium, usually present as chloride in the oil, vaporizes and reacts with sulfur oxides either in the gas stream or after deposition on tube surfaces.

Subsequently, reactions take place between the vanadium and sodium compounds with the formation of complex vanadates having melting points lower than those of the parent compounds, for example:

$$(4) \quad Na_2SO_4 + V_2O_5 \rightarrow 2NaVO_3 + SO_3 \uparrow$$
$$\text{Melting Points} \quad 1625F \quad 1275F \quad 1165F$$

Excess vanadium or sodium in the ash deposit, above that necessary for the formation of the sodium vanadates (or vanadyl vanadates), may be present as V_2O_5 and Na_2SO_4, respectively.

The sulfur in residual fuel is progressively released during combustion and is promptly oxidized to sulfur dioxide (SO_2). A small amount of sulfur dioxide is further oxidized to SO_3 by a small amount of atomic oxygen present in the hottest part of the flame. Also, catalytic oxidation of SO_2 to SO_3 may occur as the flue gases pass over vanadium-rich ash deposits on high-temperature superheater tubes and refractories.

Oil-slag formation and deposits

The deposition of oil-ash constituents on the furnace walls and superheater surfaces has been a serious problem in recent years. This deposition, coupled with corrosion of superheater and reheater tubes by deposits, was largely responsible for the break in the trend towards higher steam temperatures that occurred in the early 1960's.

Practically all boiler installations are now designed for steam temperatures in the 1000-1015F range to minimize those problems and to avoid the higher capital costs of the more expensive alloys required in tubes, steam piping, and turbine for 1050-1100F steam conditions.

There are many factors affecting oil-ash deposition on boiler heat absorbing surfaces. These factors may be grouped into the following interrelated categories:

1. Characteristics of the fuel oil.
2. Design of the boiler.
3. Operation of the boiler.

Characteristics of fuel-oil ash

Sodium and vanadium are the most significant elements in the fuel oil because they can form complex compounds having low melting temperatures, 480-1250F, as shown in Table 10. Such temperatures fall within the range of tube-metal temperatures generally encountered in furnace and superheater tube banks of many oil-fired boilers. However, because of its complex chemical composition, fuel-oil ash seldom has a single sharp melting point, but rather softens and melts over a wide temperature range.

An ash particle that is in a sticky, semi-molten state at the tube-surface temperature may adhere to the tube if it is brought into contact by the gas flow over the tube. Even a dry ash particle may adhere due to mutual attraction or surface roughness. Such an initial deposit layer will be at a higher temperature than that of the tube surface because of its relatively low thermal conductivity. This increased temperature promotes the formation of adherent deposits. Thus, fouling will continue until the deposit-surface temperature reaches a level at which all of the ash in the gas stream is in a

Table 10
Melting points of some oil-ash constituents

Compound	Melting Point, F
Aluminum oxide, Al_2O_3	3720
Aluminum sulfate, $Al_2(SO_4)_3$	1420*
Calcium oxide, CaO	4662
Calcium sulfate, $CaSO_4$	2640
Ferric oxide, Fe_2O_3	2850
Ferric sulfate, $Fe_2(SO_4)_3$	895*
Nickel oxide, NiO	3795
Nickel sulfate, $NiSO_4$	1545*
Silicon dioxide, SiO_2	3130
Sodium sulfate, Na_2SO_4	1625
Sodium bisulfate, $NaHSO_4$	480*
Sodium pyrosulfate, $Na_2S_2O_7$	750*
Sodium ferric sulfate, $Na_3Fe(SO_4)_3$	1000
Vanadium trioxide, V_2O_3	3580
Vanadium tetroxide, V_2O_4	3580
Vanadium pentoxide, V_2O_5	1275
Sodium metavanadate, $Na_2O \cdot V_2O_5 (NaVO_3)$	1165
Sodium pyrovanadate, $2Na_2O \cdot V_2O_5$	1185
Sodium orthovanadate, $3Na_2O \cdot V_2O_5$	1560
Sodium vanadylvanadates, $Na_2O \cdot V_2O_4 \cdot V_2O_5$	1160
$5Na_2O \cdot V_2O_4 \cdot 11V_2O_5$	995

* Decomposes at a temperature around the melting point.

molten state so that the surface is merely washed by the liquid without freezing and continued buildup.

In experimental furnaces it has been found that the initial rate of ash buildup was greatest when the sodium-vanadium ratio in the fuel oil was 1 to 6, but an equilibrium thickness of deposit (⅛ to ¼ in. thick) was reached in approximately 100 hours of operation. When the fuel oil contained more refractory constituents such as silica, alumina, and iron oxide in addition to sodium and vanadium, an equilibrium condition was not reached and the tube banks ultimately plugged with ash deposits. However, these ash deposits were less dense, i.e., more friable than the glassy slags encountered with a 1 to 6 sodium-vanadium fuel oil. Both the rate of ash buildup and the ultimate thickness of the deposits are also influenced by physical factors such as the velocity and temperature of the flue gases and particularly the tube-metal temperature.

In predicting the behavior of a residual oil insofar as slagging and tube-bank fouling are concerned, several fuel variables are considered including (1) ash content, (2) ash analysis, particularly the sodium and vanadium levels and the concentration of major constituents, (3) melting and freezing temperatures of the ash, and (4) the total sulfur content of the oil. Applying this information in boiler design is largely a matter of experience.

Boiler design

Generally speaking, progressive fouling of furnaces and superheaters should not occur if the tube-metal temperatures do not exceed 1000F. If such trouble is encountered, the solution can usually be found in improving combustion conditions in the furnace and/or modifying the sootblowing procedures.

Studies on both laboratory and field installations have shown that the rate of ash deposition is approximately

proportional to the velocity and temperature of the flue gases, and the concentration of oil-ash constituents in the flue gases. The geometry of the furnace and the spacing of tubes in the convection banks are selected in the design of a boiler to minimize the rate of deposition. It is common practice to use in-line tube arrangements with progressively wider lateral spacings for tubes located in higher gas-temperature zones. This makes bridging of ash deposits between tubes less likely and facilitates cleaning of tube banks by the sootblowers.

Boiler operation

Poor atomization of the fuel oil results in longer flames and frequently increases the rate of slag buildup on furnace walls which, in turn, makes it more difficult to keep the convection sections of the boiler clean. Completing combustion before the gases pass over the first row of tubes is especially important. Relatively large carbonaceous particles have a far greater tendency to impinge on the tubes than do the smaller ash particles. If these larger particles are in a sticky state, they will adhere to the tubes where oxidation will proceed at a slow rate with consequent formation of ash. Fouling from this cause is difficult to detect by inspection during boiler outages because the carbonaceous material has usually disappeared completely. It can generally be detected during operation since flames are usually long and smoky and sparklers may be carried along in the flue gases.

Regular and thorough sootblowing can have a decisive effect on superheater and reheater fouling. To be fully effective, however, sootblowing cycles should be

frequent enough so that ash deposits cannot build up to a thickness where their surfaces become semi-molten. If this point is reached, complete removal of the ash deposit can be very difficult because the sootblowers now have a dual task to perform: (1) to cool the surface of the deposit below its freezing temperature and (2) to shatter the now solid mass of slag and break its bond to the tube surface. In instances of extreme slagging, it is sometimes necessary to relocate sootblowers, install additional sootblowers to control deposition in a critical zone, or to use additives.

The boiler load cycle can also have a significant effect on the severity of slagging and superheater fouling. A unit that is base-loaded for long periods is more apt to have fouling problems on a borderline fuel oil than a unit that takes daily swings in load. In the latter instance, the furnace generally remains cleaner due to periodic shedding of slag, with the result that the gas temperatures through the superheaters are appreciably lower. This eases the burden on the sootblowers and goes a long way towards controlling ash-deposit formation in the superheater-reheater tube banks. Overloading the boiler, even for an hour or two a day, should be avoided, especially if excess air has to be lowered to the point where some of the burners are starved of air. The furnace is apt to become slagged and ash deposition creeps into the superheater and reheater tube banks.

Oil-ash corrosion

High-temperature corrosion

The sodium-vanadium complexes, usually found in oil-ash deposits, are corrosive when molten. The corrosion mechanism is probably one of accelerated oxidation of metal brought about by oxygen transfer to its surface by the constituents in the molten ash, accompanied by the removal by the ash of the normal protective oxide coating on the metal surface.

Corrosion can also be caused by sulfate attack, particularly when sodium (or some other) chloride is also present in the fuel oil, and this may occur at metal temperatures as low as 1000F. This type of corrosion is more apt to be encountered on boilers burning a low-vanadium fuel oil but containing several hundred ppm of sodium chloride. Even when the chloride content of the fuel oil is negligible, sulfate corrosion may still be severe when reducing or alternating oxidizing-reducing conditions prevail around the tubes.

A measurable corrosion rate can be observed over a wide range of metal and gas temperatures, depending on the amount and composition of the oil-ash deposit. Fig. 28 shows the combined gas and metal temperature effects on corrosion for a specific fuel oil composition of 150 ppm vanadium, 70 ppm sodium, and 2.5% sulfur. As the vanadium concentration of the fuel oil varies, the amount of corrosion, compared to a 150-ppm vanadium fuel, will increase or decrease according to the curve shown in Fig. 29.

The effect of the sodium level in the fuel oil is not quite so clear-cut because combustion conditions and the chloride content of the fuel oil may be controlling. The sodium content does, however, definitely affect the minimum metal temperature at which corrosion will be significant.
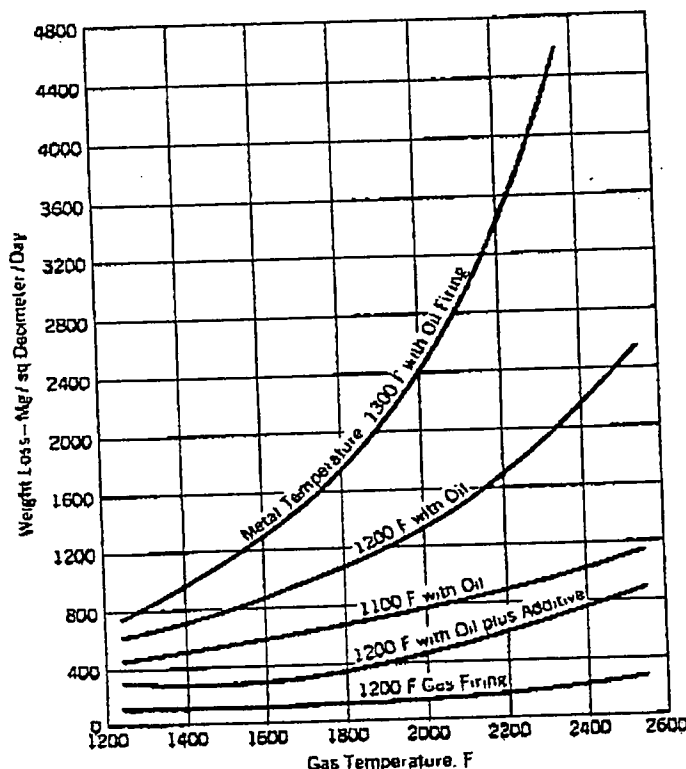

Fig. 28 Effect of gas and metal temperatures on corrosion of 304, 316, and 321 alloys in a unit fired with oil containing 150 ppm vanadium, 70 ppm sodium, and 2.5% sulfur. Test duration 100 hours.
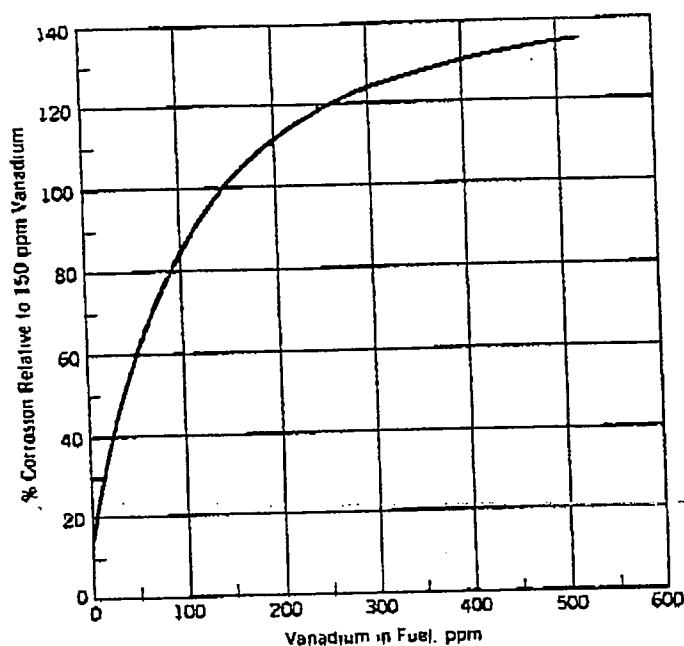
Fig. 29 Effect of vanadium concentration on oil-ash corrosion.

At the present time there does not appear to be any alloy that is immune to oil-ash corrosion. In general, the higher the chromium content of the alloy the more resistant it is to attack. This is the main reason for the use of 18Cr-8Ni alloys for high-temperature superheater tubes. High chromium contents, greater than 30%, give added corrosion resistance but at the expense of physical properties; 25Cr-20Ni has been used as a tube cladding but even this alloy has not provided complete protection. The presence of nickel in high-temperature alloys is needed for strength. High-nickel alloys may be fairly resistant to oil-ash attack under oxidizing conditions but they are liable to sulfide attack brought about by local reducing conditions or by the presence of chloride in the ash deposit. Since it is difficult to avoid such conditions entirely, high-nickel content of alloys may be of limited value. In any event, the higher material cost must be justified by longer life, which is not always predictable.

Low-temperature corrosion

In oil-fired boilers the problem of low-temperature corrosion resulting from the formation and condensation of sulfuric acid from the flue gases is similar to that previously described for coal firing.

Oil-fired boilers are more susceptible to low-temperature corrosion than are most coal-fired units for two reasons: (1) the vanadium in the oil-ash deposits is a good catalyst for the conversion of SO_2 to SO_3 and (2) there is a smaller quantity of ash in the flue gases. Ash particles in the flue gas reduce the amount of SO_3 vapor in the gas. Since oil has considerably less ash than coal, significant differences would be expected. Furthermore, coal ash is more basic than oil ash and tends to neutralize any acid deposited, oil ash generally lacks this capability.

Under certain conditions, oil-fired boilers may emit acidic particulates from their stacks that stain or etch

painted surfaces in the neighborhood of the plant. The acidic deposits or smuts are generally caused by metallic surfaces (air heaters, flues and stacks) operating well below the acid dew point of the flue gases or by soot which has absorbed sulfuric acid vapor in its passage through the boiler. Methods that can be used to prevent acid-smut emission include:

1. Minimize SO_3 formation in the flue gases,
2. Neutralize SO_3 in flue gases,
3. Maintain all surfaces in contact with the flue gases above about 250F and,
4. Completely burn fuel oil to eliminate soot particles.

Methods of control

The methods of control that have been used or proposed to control fouling and corrosion in oil-fired boilers are summarized in Table 11, but in every instance economics governs their applicability. There is no doubt that reducing the amount of ash and sulfur entering the furnace is the surest means of control, and that minimizing the effects of the ash constituents, once they have deposited on the tubes, is the least reliable. Since the severity of fouling and corrosion depends not only on the fuel-oil characteristics but also on boiler design and operating variables, a generalized solution to these problems cannot be prescribed.

Table 11
Classification of methods for controlling fouling and corrosion in oil-fired boilers

	Fuel Oil Supply
Reduce amount of fuel ash constituents to the furnace	{ Selection, Blending, Purification
	Design
Minimize amounts of fuel ash constituents reaching heat transfer surfaces	{ Furnace geometry, Tube bank arrangement, Metal temperature, Gas temperature, Sootblower arrangement
	Operation
Minimize effects of bonding and corrosive compounds in ash deposits	{ Load cycle, Sootblowing schedule, Combustion—Excess air, Additives, Water washing

Fuel oil supply

Although fuel selection and blending are practiced to some extent in this country, it is done to provide safe and reliable handling and storage at the user's plant rather than to avoid fouling difficulties. Since the threshold limits of sodium, sulfur and vanadium are not accurately defined for either fouling or corrosion, utilization of these means of control cannot be fully exploited.

Processes are available for both the desulfurization and de-ashing of fuel oils. Water washing of residual fuel oil has been successfully applied to a few marine-type boilers, but it is doubtful that it will be widely used because only sodium and sediment, mainly rust and

sand, are removed by the process. Use of low-sulfur, low-ash crudes and desulfurized fuel oil is expected to increase (see also Chapter 18).

Fuel oil additives

The practice of water washing out of service and, to a limited extent, in service has been beneficial in overcoming some of the troubles experienced with present oil fuels. In addition, continued study of the problem has revealed another approach that is effective where the fuel-oil ash is most troublesome. In brief, the method involves adding to the fuel or furnace small amounts of materials that change the character of the ash sufficiently to permit its removal by steam or air sootblowers or air lances.

Additives are effective in reducing the troubles associated with superheater fouling, high-temperature ash corrosion, and low-temperature sulfuric acid corrosion. Most effective are alumina, dolomite and magnesia. Kaolin is also a source of alumina. Analyses of typical superheater deposits from a troublesome fuel oil, before and after treating it with alumina or dolomite, are shown in three bar graphs at the left in Fig. 30. The results for a different oil treated with magnesia are shown in the bar graph at the right.
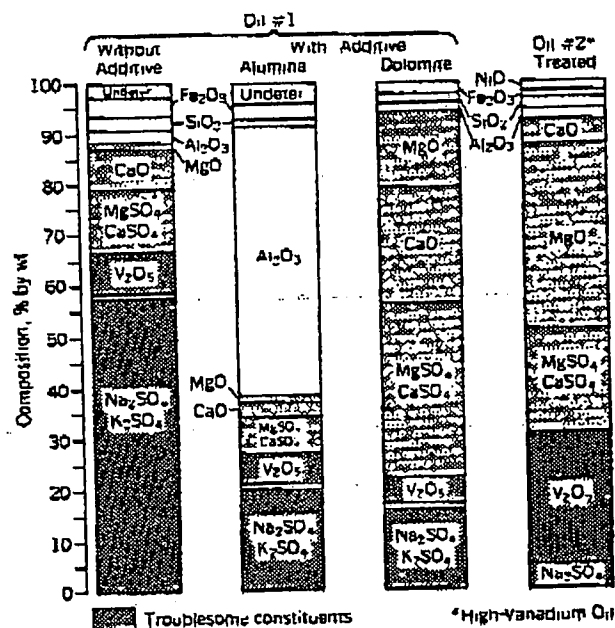

Fig. 30 Effect of fuel-oil additives on composition of oil-ash deposit.

The reduction of fouling and high-temperature corrosion is accomplished basically by producing a high-melting-point ash deposit that is powdery or friable and easily removed by sootblowers or lances. When the ash is dry, corrosion is considerably reduced.

Low-temperature sulfuric-acid corrosion is reduced by the formation of refractory sulfates by reaction with the SO_3 gas in the flue-gas stream. By thus removing the SO_3 gas, the dew point of the flue gases is sufficiently reduced to protect the metal surfaces. The sulfate compounds formed are relatively dry and easily removed by the normal cleaning equipment.

In general, the amount of additive used should be about equal to the ash content of the fuel oil. In some instances, slightly different proportions may be required for best results, especially for high-temperature corrosion reduction, in which it is generally accepted that the additive should be used in weight ratios of 2 or 3 to 1, based on the vanadium content of the oil.

Several methods have been successfully used to introduce the additive materials into the furnace. The one in general use consists of metering a controlled amount of an additive oil slurry into the burner supply line. The additive material should be pulverized to 100% through a 325-mesh screen (44 microns) for good dispersion and minimum atomizer wear.

For a boiler fired by a high-pressure return-flow oil system, it has been found advantageous to introduce the additive powders by blowing them into the furnace at the desired locations. The powder has to be 100% through a 325-mesh screen for good dispersion.

A third, and more recent method, is to introduce the additive as a water slurry through specially adapted sootblowers or lances. This method offers the advantage of applying the additive in exactly the location desired, with a possible reduction in the quantity required. Some caution should be observed with this system to prevent possible thermal shock (quench-cracking) damage to the hot tubes. The presence of chlorides in the water slurry, from either the water or the additive material, could possibly produce stress-corrosion cracking of austenitic tubing and should be considered.

The choice of the particular additive material depends on its availability and cost to the individual plant and the method of application chosen. For example, alumina
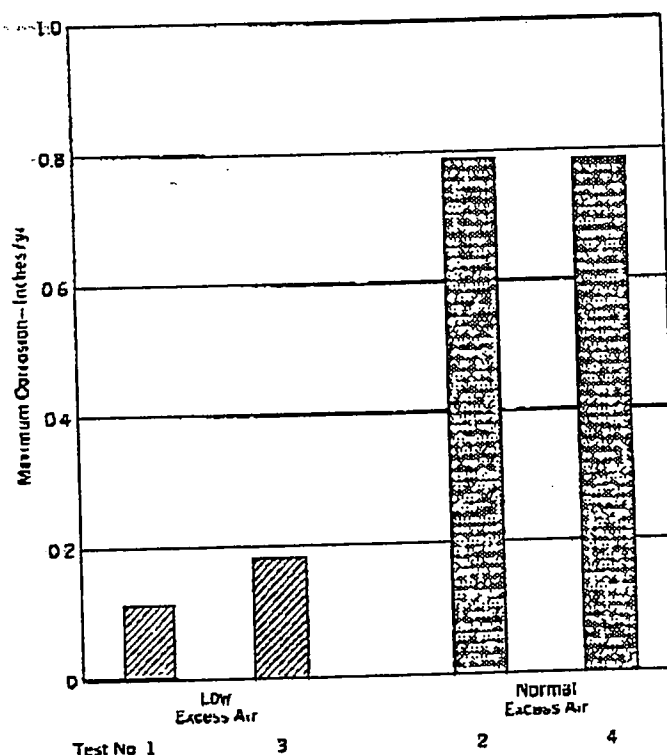

Fig. 31 Effect of low excess-air combustion on high-temperature oil-ash corrosion.

causes greater sprayer-plate wear than the other materials when used in an oil slurry.

The quantity of deposit formed is, of course, an important consideration for each individual unit from the aspect of cleaning. A comparison of the amounts of deposit formed with different additives shows that dolomite produces the greatest quantity because of its sulfating ability, alumina and kaolin form the least, and magnesia is intermediate. However, when adequate cleaning facilities are available, the deposits are easily removed, and the quantities formed should not be a problem.

Excess-air control

As mentioned previously the problems encountered in the combustion of residual fuels—high-temperature deposits (fouling), high-temperature corrosion, and low-temperature sulfuric-acid corrosion—all arise from the presence of vanadium and sulfur in their highest states of oxidation. By reducing the excess air from 7% to 1 or 2%, it is possible to avoid the formation of fully oxidized vanadium and sulfur compounds and, thereby, reduce boiler fouling and corrosion problems.

In a series of tests on an experimental boiler, it was found that the maximum corrosion rate of type 304 stainless steel superheater alloy held at 1250F in 2100F flue gas was reduced more than 75% (see Fig. 31) when the excess air was reduced from an average of 7% to a level of 1 to 2%. Moreover, the ash deposits that formed on the superheater bank were soft and powdery, in contrast to hard, dense deposits that adhered tenaciously to the tubes when the excess air was around 7%. Also, the rate of ash buildup was only half as great. Operation at the 1 to 2% excess air level practically eliminated low-temperature corrosion of carbon steel at all metal temperatures above the water dew point of the flue gases (Fig. 32). However, much of the beneficial effects of low excess-air combustion are lost if the excess air at the burner fluctuates even for short periods of time to a level of about 5%. Carbon loss values for low ex-
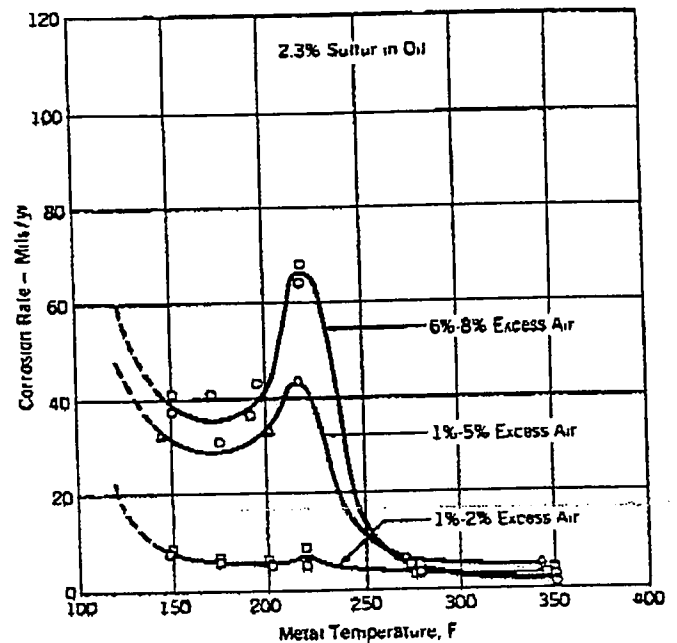

Fig. 32 Effect of excess air on low-temperature corrosion of carbon steel.

cess air were approximately 0.5%, which is generally acceptable for electric utility and industrial practice.

A number of large industrial boilers both in this country and in Europe have been operating with low excess air for several years. As a result, the benefits in reducing low-temperature corrosion are well established for units with steam temperatures of 1000F or less. However the benefits on high-temperature slagging and corrosion are not wholly conclusive. In any event, great care must be exercised to distribute the air and fuel oil equally to the burners, and combustion conditions must be continuously monitored to assure that combustion of the fuel is complete before the combustion gases enter the convection tube banks.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re the Application of:) Group Art Unit: 3749
)
    JOHNSON et al.) Examiner: RINEHART, KENNETH
)
Serial No.: 10/622,677) <u>DECLARATION OF</u>
) <u>MICHAEL DURHAM</u>
Filed: July 18, 2003) <u>UNDER 37 C.F.R. §1.132</u>
)
Atty. File No.: 3791-13-CON)

For: "LOW SULFUR COAL ADDITIVE)
      FOR IMPROVED FURNACE)
      OPERATION")

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313

Dear Sir:

    I, Michael Durham, state as follows:

    1.   I received a Bachelor of Science in Aerospace Engineering from Pennsylvania State University in 1971; a Master of Engineering in Environmental Engineering from the University of Florida in 1975; a Ph. D. in Environmental Engineering from the University of Florida in 1978; and a Master of Business Administration from the University of Denver in 1997.

    2.   I have been previously employed by the National Academy of Sciences (1972-1973), the American Psychological Association (1973-1974), Environmental Engineering Consultants (1975-1978), Denver Research Institute (1978-1985, and ADA Technologies, Inc. (1985-1996) (of which I was I founder and Executive Vice President). I am a cofounder and President of ADA Environmental Solutions, LLC, and a shareholder, President, and member of the Board of Directors of ADA Environmental Solutions, Inc. ADA Environmental Solutions, Inc., was founded in 1996 to commercialize environmental technologies to help existing coal fired-boilers meet more stringent environmental regulations. ADA Environmental Solutions,

LLC, the owner of the above patent application, is a wholly owned subsidiary of ADA
Environmental Solutions, LLC.

3.   For the past 28 years, including during my employment by Environmental
Engineering Consultants, ADA Technologies, Inc., and ADA Environmental Solutions, Inc., I
have been involved in the measurement and control of air pollution from utility and industrial
sources. The majority of this work was directed at reducing emissions of particulates, sulfur
oxides, nitrogen oxides, and mercury from coal-fired boilers.

4.   I have received numerous honors in the area of air and waste management, with
specific emphasis on coal-fired utilities. For example, from 1989 to 1990 I was Chairman of the
Rocky Mountain States Section of the Air and Waste Management Association (A&WMA), from
1994 to 1996 I was Chairman of the A&WMA National Technical Committee on Control of
Particulate Matter and Acid Gases, and from 1999 to 2002, I was Chairman of the A&WMA
Emission Control Division. I was the 2001 winner of the A&WMA Sensenbaugh Award for Air
Pollution Control Technology and the 2003 winner of an R&D 100 Award for Mercury Control
Technology for coal-fueled boilers. In 2001, I was appointed by the DOE Secretary Abraham to
the National Coal Council. I have published over 180 papers related to air pollution
measurement and control.

5.   I submit that I am qualified to testify as to the understanding of one of ordinary
skill in the relevant arts of air and waste management and utility design and operation at the time
the above-identified application and the provisional application (from which the above-identified
application claims priority) were filed.

6.   In connection with the Office Action mailed January 29, 2004, I reviewed the
following documents: (a) the Office Action; (b) U.S. Patent 6,484,651 to Shepard, Jr., et al. ("the
Shepard Patent"); (c) the above application ("the Subject Application"); and (d) U.S. Provisional
Application Serial No. 60/213,915, filed June 26, 2000, entitled "Low-Cost Technology to

Improve Operation of Cyclone Furnaces Firing Low-Sulfur Western Coals" ("Provisional Application") from which the Subject Application claims priority.

7.   At pages 3-5 of the Office Action, the Examiner states that the sub-bituminous coal limitation of dependent claims 2 and 20 of the Subject Application, namely that "the solid fuel comprises a sub-bituminous coal", fails to comply with the written description requirement of 35 U.S.C.§112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

8.   I disagree. The Subject and Provisional Applications each reference coals from the Powder River Basin of Montana and Wyoming (Provisional Application at pages 3-5 and 8; Subject Application at page 1, lines 8-11) and the Subject Application refers specifically to "sub-bituminous coal" as the solid fuel feed (Subject Application at page 6, line 9). Because coal in the Powder River Basin is primarily sub-bituminous coal, the reference to the Powder River Basin would convey to one skilled in the relevant art that the inventors, at the time the Provisional and Subject Applications were filed, had possession of the invention claimed in claims 2 and 20.

9.   At page 4 of the Office Action, the Examiner states that the cyclone boiler limitation of claim 5, namely that the boiler is a cyclone boiler, fails to comply with the written description requirement of 35 U.S.C.§112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

10.   I disagree. The Subject and Provisional Applications each specifically refer not only to the general class of boiler that includes the cyclone boiler, namely wet-bottom boilers, (Provisional Application at page 2; Subject Application at page 6, lines 15-18) but also

specifically to cyclone boilers (Provisional Application at pages 1-5 and 7-8 and Subject Application at Figure 1, page 1, line 24 to page 2, line 19, page 5, lines 16-17, and page 6, lines 15-18). These references would convey to one skilled in the relevant art that the inventors, at the time the Provisional and Subject Applications were filed, had possession of the invention claimed in claim 5.

11.   At page 4 of the Office Action, the Examiner states that the pulverizing limitation of claim 7, namely that the solid fuel is pulverized prior to being introduced into the boiler, fails to comply with the written description requirement of 35 U.S.C. §112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

12.   I disagree. The Subject Application discloses a "slag type" furnace in which a slag layer forms on a surface of the burner and captures coal particles for combustion. (Subject Application at page 1, lines 21-23) Both the Subject and Provisional Applications disclose a cyclone furnace or boiler *and* wet-bottom boilers as noted in Paragraph 10 above. "Pulverized" coal boilers include both wet-bottom and dry-bottom boilers using a pulverized coal feed. A cyclone boiler is a type of wet-bottom boiler for which the coal feed is crushed but not pulverized. A cyclone boiler is the only type of wet-bottom boiler which uses crushed but not pulverized coal feed. While it is true that pulverizers and crushers are differing types of devices and produce different size distributions of coal feed, the reference to the genus "wet-bottom boilers" would reasonably convey to one skilled in the relevant art that the inventors, at the time the Provisional and Subject Applications were filed, had possession of the subject matter of claim 7.

13.   At page 4 of the Office Action, the Examiner states that the subject matter of claim 12, namely that the boiler includes a pulverizer and a fuel transfer system communicating with the pulverizer and the burner, fails to comply with the written description requirement of 35

U.S.C.§112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

14.   I disagree. As noted previously, the Specifications of the Provisional and Subject Applications reasonably convey to one skilled in the relevant art that the inventors, at the time the Provisional and Subject Applications were filed, had possession of wet-bottom boilers, whether using pulverized or crushed coal feed. It necessarily follows that the pulverizer is located upstream of the combustion chamber. The burner is disclosed at page 2 of the Provisional Application and in Figure 1 of the Subject Application. The fuel transfer system is disclosed at page 7 of the Provisional Application and in Figures 4-5 and pages 14, lines 7-13 (coal feed pipes 244a,b) and 17, lines 14-15 (coal feed lines 344a,b). Finally, the combustion chamber is described at page 2 of the Provisional Application and in Figure 1 and at page 1, line 28, and page 2, lines 7-9, (combustion chamber 108) of the Subject Application.

15.   I have reviewed proposed Figure 9 and find it to be supported by both the Provisional and Subject Applications.

16.   For at least the reasons set forth above, the subject matter of claim 12 is described in the Specifications of both the Provisional and Subject Applications in such a way as to reasonably convey to one skilled in the relevant art that the inventors, at the time each of the applications was filed, had possession of the claimed invention.

17.   At page 4 of the Office Action, the Examiner states that the subject matter of claim 14, namely that the concentration of iron-bearing material to solid fuel is from about 0.5 to about 2.5 weight percent, fails to comply with the written description requirement of 35 U.S.C.§112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

18.   I disagree. The Provisional Application discloses, at page 8, a concentration of iron-bearing material to solid fuel of 20 lb/ton or 1 wt.%. The Subject Application discloses at page 9, lines 6-7, iron-bearing concentrations relative to the solid fuel of 10 lb/ton (or 0.5 wt.%), 20 lb/ton (or 1.0 wt.%), and 50 lb/ton (or 2.5 wt.%). For at least the reasons set forth above, the subject matter of claim 14 is described in the Specifications of both the Provisional and Subject Applications in such a way as to reasonably convey to one skilled in the relevant art that the inventors, at the time each of the applications was filed, had possession of the claimed invention.

19.   Finally at page 5 of the Office Action, the Examiner states that the subject matter of claim 29, namely that the concentration of carbon-containing compound in the iron bearing material is from about 0.1 to about 10 weight percent, fails to comply with the written description requirement of 35 U.S.C.§112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

20.   I disagree. This precise concentration range is disclosed in the Subject Application at page 12, lines 17-18, which discloses that the additive can include "from about 0.1 to about 10 wt.% (dry basis) greases and oils." The Provisional and Subject Applications further disclose additive carbon compound concentrations within this range at page 8 of the Provisional Application and page 15, lines 2-4, of the Subject Application (boiler slag in a concentration of about 2 to a about 20 wt.% and more preferably of about 2 to about 10 wt.%). The Subject Application discloses at page 13, lines 10-13, the addition of xanthium gum (or another organic adhesive) in a ratio of about 100:1 (or 1 wt.%) to 1000:1 (or 0.1 wt.%) parts additive to part adhesive.

21.   For at least the reasons set forth above, the subject matter of claim 29 is described in the Specifications of both the Provisional and Subject Applications in such a way as to

reasonably convey to one skilled in the relevant art that the inventors, at the time each of the applications was filed, had possession of the claimed invention.

22.   I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully submitted,

Date: _July 29 2004_   By: _____
／ Michael Durham

EXHIBIT 2

Coal Properties, Sampling & Ash Characteristics
by Rod Hatt
Coal Combustion, Inc.
Versailles, KY
859-873-0188

Introduction

The Powder River Coal is classified as sub-bituminous ranked coal. Coal rank is an indication of how much transformation the original plant material has under gone. The American Society for Testing and Materials (ASTM) defines coal rank for lignite and PRB type coals using the heating or Btu value expressed in a moisture, ash free (maf) basis. This basis eliminates the impacts of ash and moisture levels on the heating value. The heating value is used for lower ranked coals, the maf volatile is used to classify higher ranked bituminous and anthracite type coals. The first phase of coalification (fossilization) is to preserve the plant material from oxidation. This peat moss like material is still basically plant material. The first coal like material formed is lignite, or brown coal. The coalification process basically squeezes out *oxygen* and *water.* As the plant material becomes less like wood and more like oil, the pore structure constricts limiting the water retention capacity of a coal. This water retention capacity is measured using the equilibrium moisture (EQ moisture) test. Sub-bituminous coals like the PRB coals are the next step in the coal ranking system. Then comes the low ranked Bituminous C type coal. This is the ranking of many Illinois Basin coals. The higher ranked Bituminous B and C coals are generally found in the Appalachian coalfields.

Most of the coal tests that ASTM has standardized were written around higher ranked bituminous and anthracite coals. The tight pore structures of these coals limited the amount of inherent moisture they could hold. Typically these high ranked coals have EQ moistures of 1-10. The first step of determining coal quality in the lab is to air-dry the sample to near equilibrium with the laboratory humidity levels. This is done to minimize any impact on lab results of additional drying or absorption of water from the air. In high rank coals, the moisture lost in the air-drying step is near equivalent to the surface moisture.

The residual moisture is that moisture that is still locked up in the coal after air-drying. The higher ranked coals that ASTM standards were based on possess this well-defined split between the air-dried or surface moisture and the residual or near EQ moisture. This is not the case for low rank coals like PRB coal. The sponge-like or wood like nature of PRB coals make the split between surface moisture and inherent moisture a rather fuzzy line.

Quality

Most of the quality differences between PRB coal and the higher ranked coal can be explained by understanding that the PRB coal has this looser pore structure and additional moisture retention capacity. PRB coal also has more oxygen chemically bonded to the coal.

Quality Table

Btu/lb..	Higher moisture and oxygen result in lower Btu/lb.
Sulfur	The low sulfur nature of PRB coal is due to fresh water exposure rather than sea water.
Volatile	High volatile nature due to low rank has many oxygenated compounds like CO.
Ash	Low inherent ash has large non-rock or organically bound calcium and sodium fraction.
HGI	near mid fifties as seen by mills, hare to measure accurately due to moisture impacts.
Fusion	Generally low fusion due to high CaO content. Does not predict ash deposits as well as in eastern US coals.
Ash Chemistry	Sulfur Trioxide SO3 is high due to capture of sulfur by calcium in ash. This can bias the percent ash compared to actual amount of fly ash and bottom ash produced.

Chemical Fractionation
Fouling Deposits
Ash Viscosity
Abrasion
Spontaneous Combustion

Sampling

The sampling of PRB coal is a little harder to do properly due to the coal's ability to gain and lose moisture. This requires good ribbon flow and a tight sampler. Use the ASTM requirements for raw coal, as out of seam dilution is a main component of higher ash products. Clean sampler regularly to avoid coal build-up and fire hazzards.

Causes of Ash Deposits

The main causes of ash deposits depend where you work. If you work in steam plant operations the main cause is lousy coal, if your are a coal buyer the main cause is lousy steam plant design, and if you are in engineering the main cause is lousy steam plant operation. All are right in a sense. Scientific analytical investigations reveal that it is usually a combination of all three of these areas.

The following table presents the major causes of ash deposits:

TABLE I - Major Causes of Ash Deposits

Fuel Related	Large pyrite particles that impact the furnace wall before they completely combust
	Clay minerals that contain significant amounts of iron, calcium, sodium or potassium causing them to have low melting temperatures
	Interaction of pyrite, clays and akalis with alumino silicates to form low viscosity melts
	Extremely fine or organically bound alkalis
Equipment Related	Soot blowers not in operation or used improperly
	Poor pulverization of fuel
	Improper air to fuel ratio
	Burners damaged or improperly adjusted
	Changes in operation of boiler or other equipment

Design Related   Furnace size too small for fuel

         Tube material and/or spacing inadequate

         Soot blowing coverage inadequate

         No means provided to observe slag buildup

Analytical Procedures

Slag

Lets start our review with an overview of coal mineralogy and its relationship to coal ash chemistry, melting & slagging properties, and fusion temperature. There are not distinct melting points for coal ash like with ice or other pure compounds, so when melting is mentioned it is used to represent a decrease in viscosity, rather than a melting point. When coal ash melts it occurs on both a large scale and a microscopic scale. On the large or bulk scale the ash behaves like a glass. As the temperature of the material increases, its viscosity decreases. At temperatures less than 2000° F. the ash may appear solid, or at least stiff, such as a Tootsie Roll. On a microscopic scale several minerals may have all ready melted, but their concentrations are low when compared to other minerals with higher melting temperatures. As the temperature is increased the ash becomes less viscous or more liquid like. Many reactions are now occurring between the minerals as they melt and become more fluid. As the molten components mix they become more like molten glass. This molten material starts to dissolve the non molten materials like quartz and other minerals. In this way the melting temperature of minerals such as sandstones and shales are lowered by other minerals such as pyrite and limestone.

The ASTM Fusion Temperature Test is a documented observation of this process occurring in coal ash shaped like a small cone, and placed in a furnace with increasing temperatures. The initial deformation temperature, ID, is usually a hundred or more degrees above where the first low melting temp. minerals start to melt. The

remaining fusion temperatures represent an ever increasing amount of molten material, and a lowering of the viscosity of the glass like material. It should be noted that even at the fluid temp. there may be solid or non-melted minerals such as quartz. The atmosphere of the furnace is controlled to either an oxidizing (like air) or a reducing (CO present) condition. This is important due to the oxidation behavior of iron (Fe) atoms. Reduced iron lowers melting and fusion temperatures of ash much better than the oxidized form. In coals that have significant iron levels, like those in the Illinois Basin, the oxidation state of the iron is critical. The difference between the oxidizing and reducing fusion temps. can be hundreds of degrees. This phenomenon is one of the variables that make consistent fusion temperature data hard to obtain.

When trying to determine the behavior of coal ash in a boiler, both the type and size of minerals present is important information. Unfortunately it is both difficult and expensive to determine the actual minerals in coal. The ash chemistry or major and minor elements in coal ash are the next most useful information. This is because melting properties can be estimated and minerals can be inferred. Although the cost of ash chemistry is higher than fusion tests, the information obtained is well worth the expense. The fusion temperature test is a lower cost technique with reasonable turnaround time. Fusion temperatures have been used for years, and are contained in most coal contracts. Unfortunately, fusion temps provide no mineralogical information, are notoriously imprecise and are influenced by all sorts of factors that cause variability. It is the author's experience that different laboratories can produce fusion temperatures that vary well outside the ASTM guidelines, and both laboratories are performing satisfactorily.

Analytical Procedures
Ash levels

Ash levels in coal are generally reported from the lab as a percent of ash. This is convenient for the lab but not completely representative of what the boiler sees. Boilers demand Btus, not tons of fuel. A more representative (for the boiler) way to express ash levels is to use pounds of

ash per million Btu. These units are easy to calculate using the following expression:

Lb. Ash/MBtu = %Ash/(Btu/lb./10,000)

Ash fusion temperatures

Ash fusion temperature tests have been around for almost a century. At first there was just one History
Stoker furnaces
Deficiencies **Does not work well with PRB coals**
Reducing vs. Oxidizing conditions
Advanced ash fusion techniques

Ash Chemistry
Not Minerals, just oxides

Acids or glass formers
Silicon dioxide	SiO2
Aluminum oxide	Al2O3
Titanium dioxide	TiO2

Bases or fluxing agents
Iron oxide	Fe2O3
Calcium oxide	CaO
Magnesium oxide	MgO
Potassium oxide	K2O
Sodium oxide	Na2O

Base to acid ratio
Sum of bases/sum of acids
B/A vs. Fusion Temps.

Slagging index
Dry sulfur x B/A
Iron squared term
Elemental loading
Pounds of iron per million Btu
Pounds silica and other elements

Computer Controlled Scanning Electron Microscopy

Fouling Deposits

Most fouling problems caused by Calcium sulfate deposits

  Chemical Fractionation
    Active alkali
      Water soluble
      Ammonium Acetate soluble
      Weak acid soluble
      Micro crystals

Cyclone and Wet Bottom Furnaces
  Each cyclone is individual furnace
  Balanced air to fuel ratio
  Must have wet slag to work
    Must be hot, maintain minimum loading
    Coal Sizing
    Ash loading minimum
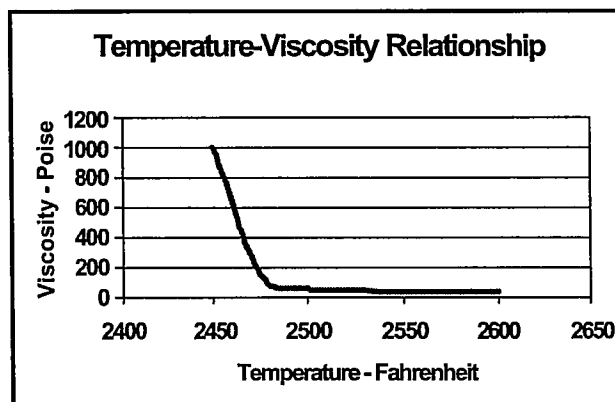   Must be low fusion ash
      Many don't use fluid fusion temperature
      T-250 temperatures
        Temperature at which slag will flow
        T-250 methods
        T-250 vs. Heating value

Temperature-Viscosity Relationship

Ash Viscosity Measurement

Deposit Analyses
  Proper Sampling (2)
  Optical and Electron Microscopy

EXHIBIT 3

US006484651B1

(12) **United States Patent**
Shepard, Jr. et al.

(10) Patent No.: **US 6,484,651 B1**
(45) Date of Patent: **Nov. 26, 2002**

(54) **METHOD FOR OPERATING A SLAG TAP COMBUSTION APPARATUS**

(75) Inventors: **Robert N. Shepard, Jr.**, Winfield, WV (US); **Peter L. Rozelle**, Forty Fort, PA (US)

(73) Assignee: **Crown Coal & Coke Co.**, Pittsburgh, PA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/684,125**

(22) Filed: **Oct. 6, 2000**

(51) Int. Cl.[7] **F23B 7/00**

(52) U.S. Cl. **110/342; 110/342; 110/345; 122/235.26**

(58) Field of Search .... 122/235.26, 4 D; 165/104.16; 110/218, 219, 234, 236, 263, 266, 341, 342, 343, 346, 347

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Primary Examiner—Ira S. Lazarus
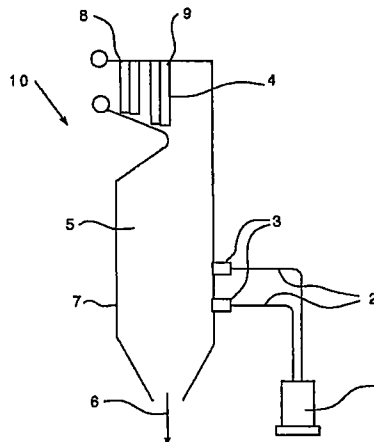*Assistant Examiner*—K. B. Rinehart
(74) *Attorney, Agent, or Firm*—Kirkpatrick & Lockhart LLP

(57) **ABSTRACT**

The present invention provides a method of operating a solid fuel fired boiler comprising introducing a solid fuel and an iron-bearing material into the boiler. The solid fuel is at least partially combusted in the boiler to produce an ash slag, wherein the ash fusion temperature characteristics (i.e., one or more of the IDT, ST, HT, and FT) of the ash slag are different than the ash fusion temperature characteristics of the ash slag that would result on combustion of the solid fuel alone. The method of the present invention is particularly applicable to slag tap boilers, including cyclone-type boilers. These boilers are, typically, designed to operate with a liquid ash slag.

The iron-bearing material may be, but is not limited to, at least one of iron ore beneficiation tailings, iron ore fines, pelletized blends of coal and iron-bearing material, pelletized solid fuel containing iron-bearing compounds, iron-bearing boiler ash, mill scale from steel production, dust from blast furnace gas cleaning equipment, flue dust from sinter plants, and other materials including iron or including material that bears iron. According to the present invention also describes methods of introducing the iron-bearing material into the slag tap combustion apparatus. The method of the invention allows lower sulfur coals, as well as other fuels typically unsuited for use in slag top boilers, to be used in such boilers, significantly reducing SO_2 emissions.

26 Claims, 5 Drawing Sheets

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FIG. 1

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20   21

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12A

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12B   14

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FIG. 2

FIG. 3

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FIG. 4

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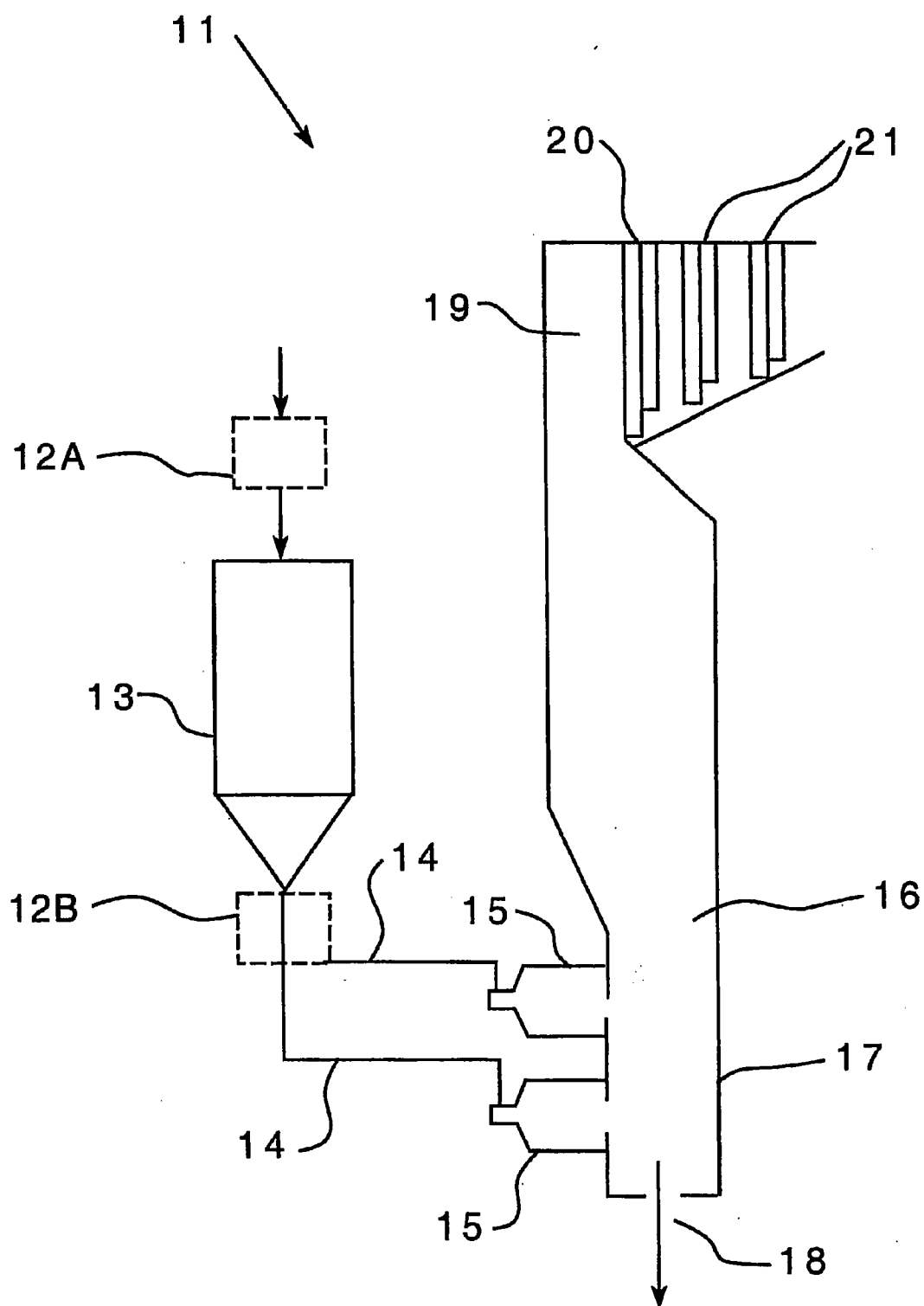
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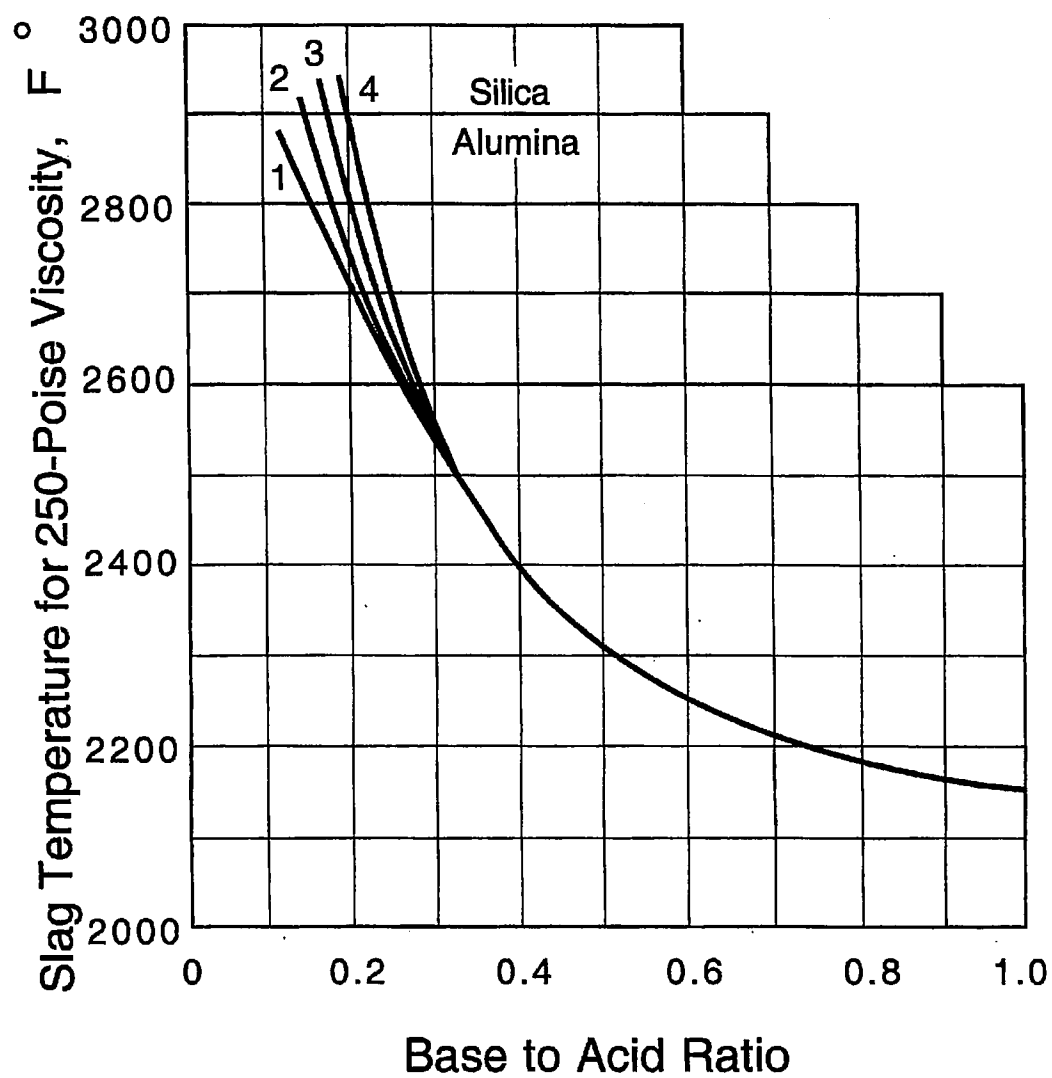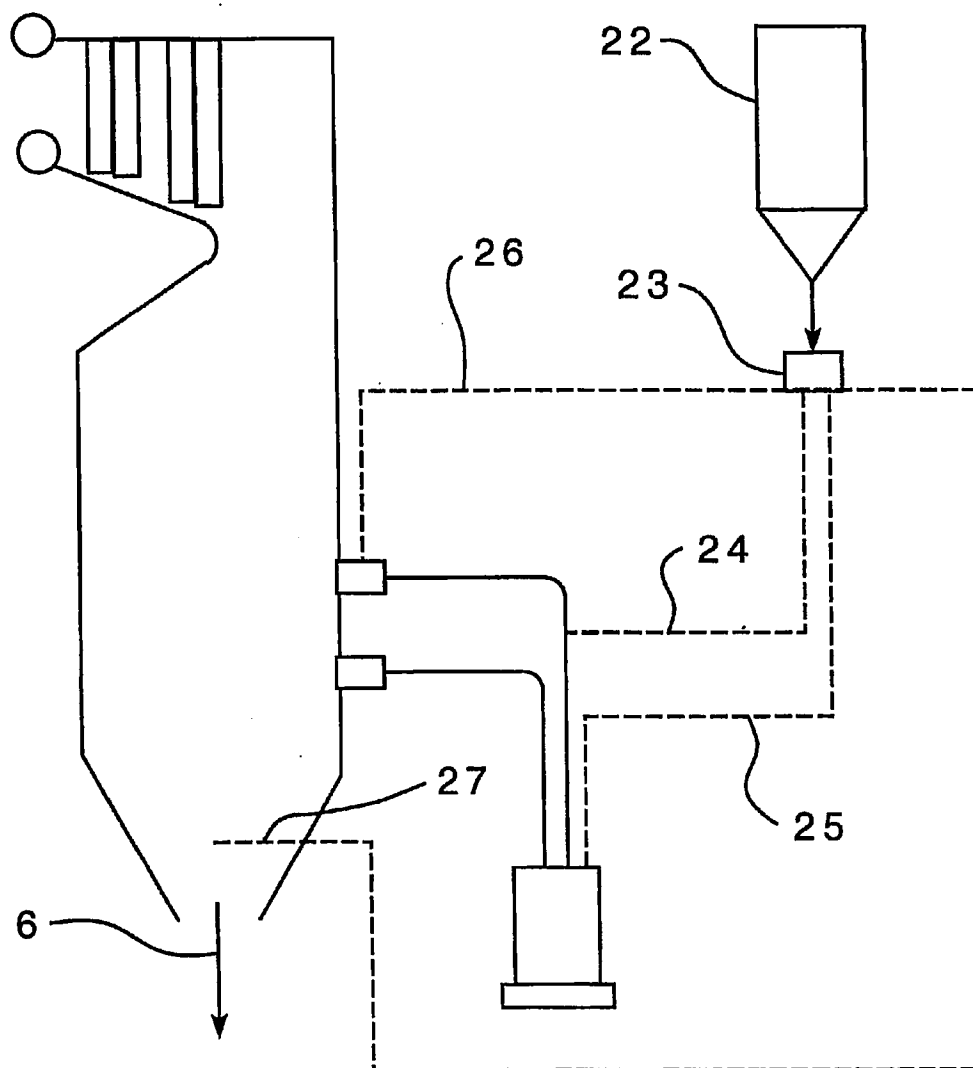
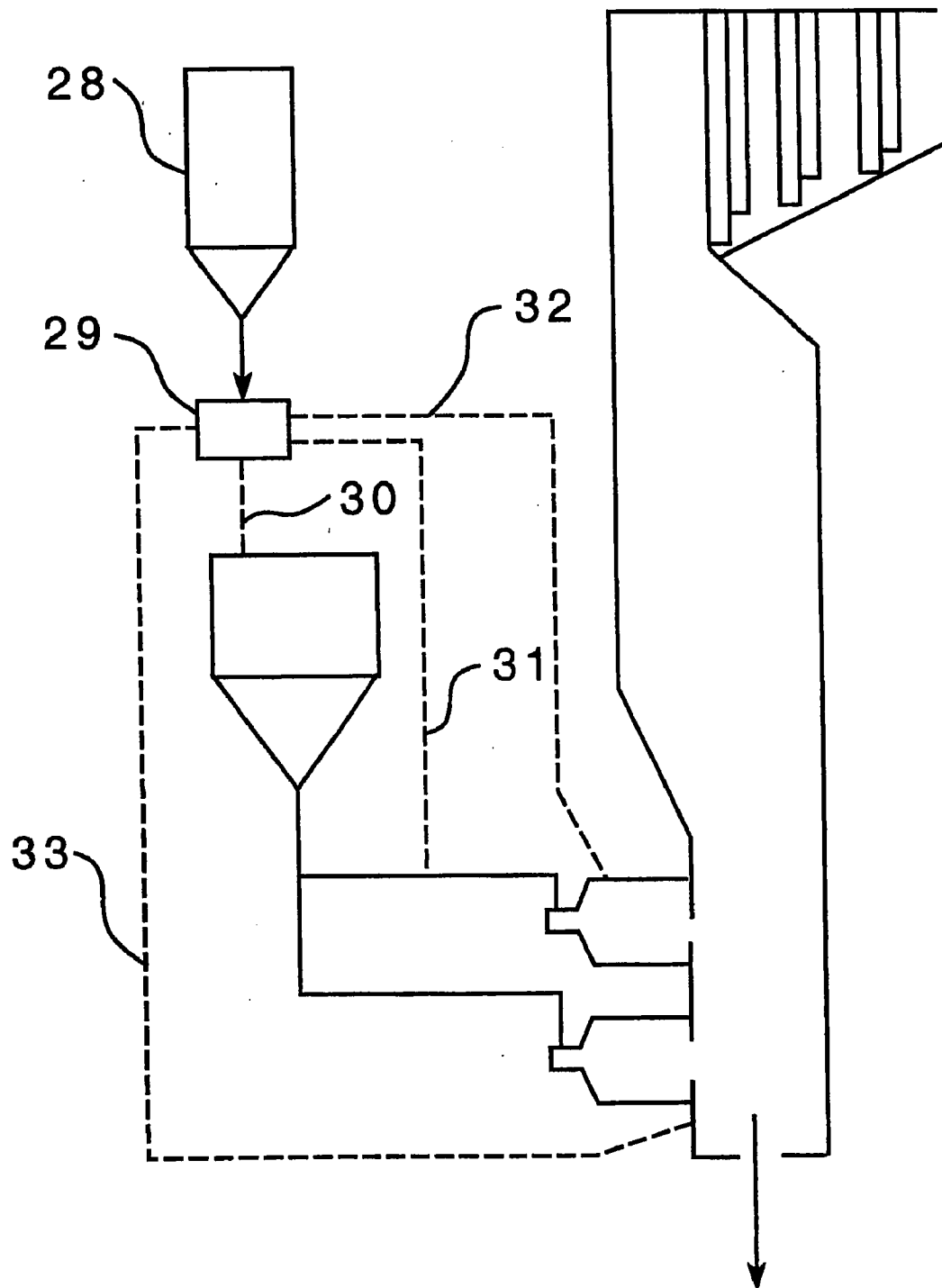# FIG. 5

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METHOD FOR OPERATING A SLAG TAP COMBUSTION APPARATUS

CROSS-REFERENCE TO RELATED APPLICATIONS

Not Applicable

FEDERALLY SPONSORED RESEARCH

Not Applicable

TECHNICAL FIELD AND INDUSTRIAL APPLICABILITY OF THE INVENTION

The present invention is directed to the operation of slag tap-type combustion apparatuses for the production of steam, generation of electric power, or for any other purpose. Application of the present invention to solid fuel-fired slag tap-type boilers will allow a reduction in noxious emissions of these boilers. More particularly, the present invention is directed to the addition of iron-bearing compounds to solid fuel-fired slag tap-type boilers for the purpose of fluxing the ash of fuels that would otherwise produce ash slag with high ash fusion temperatures and/or high viscosity, or that would otherwise be incompatible, for environmental or other reasons, with such boilers. As described in detail below, many different industrial products and by-products may be used as the iron-bearing compounds utilized in the method of the present invention. The method of the present invention may be used in heat, steam, and power production, and in any other applications of solid fuel-fired slag tap-type boilers.

BACKGROUND OF THE INVENTION

The combustion of solid fuel releases energy that may be harnessed for the production of heat, steam, electricity, or for other purposes. Solid fuels presently combusted for the production of heat, steam, electricity, or other purposes include, but are not limited to, coal, biomass, petroleum coke, and other synthetic fuels. The most widely used solid fuel for electricity generation is coal. Coal is a macromolecular network composed of groups of polynuclear aromatic rings, to which are attached subordinate rings connected by oxygen, sulfur, and aliphatic bridges. Combustion of the organic matter of the macromolecular network generates heat that typically is used to generate steam that drives steam turbines and generates electricity. Along with the generation of heat, combustion of coal produces flue gases and fuel ash slag. The ash slag generally consists of the mineral matter remaining after combustion of the organic matter in the coal. Thus, the slag may include, for example, silicas, aluminas, iron oxides and other inorganic compounds.

Coal is abundant in the United States, more abundant than oil, for example, and coals from different regions of the United States and the world have different characteristics, such as chemical composition, heat value, and physical properties. Much of the coal from the eastern region of the United States has a high sulfur content and when combusted produces an ash that can be handled as a liquid at conventional combustion chamber temperatures. Conversely, low sulfur coal from the eastern region of the United States produces an ash that cannot be handled as a liquid at these temperatures, due to elevated melting temperatures. Handling low-sulfur coal from the western United States may present handling problems similar to those encountered with

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eastern region low sulfur coals, or they may present operational difficulties due to unfavorable slag viscosity characteristics.

Certain boiler systems that are fired with solid fuels, and more particularly fired with coal, are designed to operate with a continuous flow of liquid fuel ash or "slag" out of the bottom region of the boiler. Boilers of this type are variously referred to as "slag tap" or "wet bottom" boilers. The operation of these boilers is limited to coals that combustion produce an ash slag having a low ash fusion temperature (AFT), low viscosity, or other characteristic that allows the ash slag to flow from the combustion chamber of the boiler during operation of the boiler. The ash fusion temperature properties of the resultant fuel ash slag may be characterized in a number of ways, including initial deformation temperature (IDT), softening temperature (ST), hemispherical temperature (HT), and fluid temperature (FT). The AFT properties are commonly determined by the procedure outlined in ASTM Standard D-1857. This procedure defines the IDT as the temperature at which the first rounding of the tip of a cone formed from the ash of the coal being evaluated occurs; the ST is defined as the temperature at which the cone has fused down to a spherical lump having a height equal to the width of the base; the HT is defined as the temperature at which the cone has fused down to a hemispherical lump having a height which is one half the width of the base; and the FT is defined as the temperature at which the fused mass has spread out in a nearly flat layer with a maximum height of one sixteenth of an inch. In this specification, these temperatures are collectively referred to as the Ash Fusion Temperature or AFT characteristics of a particular ash.

Slag tap boilers fall into two general categories, both requiring production of a liquid ash slag from combustion of the solid fuel to operate properly. The first category is characterized by boilers that fire the fuel in pulverized form. Such boilers are referred to herein as "pulverized fuel" boilers. The second category includes boilers commonly referred to as cyclone boilers. In a cyclone boiler, crushed coal is fed into the burner end of a water cooled, horizontally oriented cylinder. Combustion air is introduced into the cylinder tangentially to impart a whirling motion to the coal. Coal fired boilers in both of these broad categories require the use of coal that produces an ash with properties characteristic of low AFT and favorable viscosity properties over the temperature range experienced in the combustion environment. Such AFT and viscosity properties are necessary to allow the ash slag to flow from the boiler. Typically, coals and other fuels with the low AFT characteristics or favorable ash viscosity properties required for use in slag tap boilers also have high sulfur concentrations. High sulfur content coals and other fuels produce greater sulfur dioxide and noxious gases when combusted in fuel-fired boilers.

Slag tap boilers are typically individually designed to burn coal from the local area. Therefore, the combustion chamber is designed to operate with the particular ash produced from a certain coal type. Conversely, coal meeting certain predetermined specifications must be used in each slag type boiler to ensure proper operation. These specifications include, but are not limited to, specifications for AFT characteristics, ash slag viscosity temperature profile range, ash slag base-to-acid ratio, as well as others. Coals which do not meet the specifications engineered into a certain designer's slag tap boiler cannot be used in the boiler.

Phase I of the Acid Rain Program of the 1990 Clean Air Act placed a limit on the amount of sulfur dioxide (SO_2) that can be emitted annually by certain sources. SO_2 emissions from coal fired electric utility plants located in the eastern

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and midwestern states were typically limited to a greater degree than other sources. Sources of SO_2 air pollution are allocated allowances, or "rights to pollute", based on their historic level of SO_2 emissions. Each allowance permits one ton of SO_2 to be released into the air and cannot be used again. At the end of each year, polluting sources must hold enough allowances to cover their SO_2 emissions for that year. Any remaining allowances can be sold, traded, or banked for future use. If a source of air pollution does not have enough allowances to cover its SO_2 emissions, it can buy allowances on the open market. Every year the limit on the amount of SO_2 that can be emitted annually is reduced. Allowances are, therefore, a valuable commodity and emissions of SO_2 are becoming more expensive every year. Phase II of the Acid Rain Program, which began in the year 2000, further tightens the annual SO_2 emission limits imposed on coal fired utilities and on smaller, cleaner burning plants.

Therefore, burning of high sulfur coals has become or will shortly become cost prohibitive for many electric or steam generation facilities. Since slag tap or cyclone boilers were designed to operate using high sulfur coals with low AFT characteristics, continued operation of these facilities using high sulfur coals and conventional power production methods will continue to become increasingly costly, to producers and consumers alike. Lower sulfur coals generally have ash chemistry and AFT characteristics that are outside the range for which these boilers were originally designed and, therefore, use of these alternate fuels can cause significant operational problems. For example, lower sulfur coals typically have higher AFT characteristics (i.e., higher IDT, ST, HT, and FT) and, therefore, the resultant fuel ash may not flow from the bottom of the boiler, a requisite with slag tap boilers.

In order to address the problems associated with the use of alternate coal types in slag type boilers, attempts have been made to modify the AFT characteristics of coals. For example, U.S. Pat. No. 5,364,421 describes a process wherein bituminous coal, which is unsuitable for use in slag tap boilers, is blended with lignitic coal. The blend is adjusted such that the resultant fuel ash has a viscosity at or below 250 poise at 2600° F., the operating temperature of the combustion chamber. The '429 patent states that coals having ash viscosity in this range are suitable for use in slag tap boilers. However, the technique of blending coals to adjust AFT characteristics has major limitations because the amount of high sulfur coal that can be blended with low sulfur coal and still operate with the sulfur emissions regulations is limited. Also, the blending of coals has only a limited effect on the properties of the ash slag. Therefore, this method has limited industrial applicability.

Thus, there exists a need for a method of modifying the operation of solid fuel-fired slag tap boilers to allow the boilers to operate with alternate fuels for which the boilers were not designed. There also exists a need for a method of altering the AFT characteristics of low sulfur coals to render them suitable for use in certain slag tap boilers.

In addition, there exists a need for a method of maintaining stable boiler operation when operating slag tap boilers with solid fuels that would produce ash slag with AFT characteristics outside the range for which the boilers were originally designed.

SUMMARY OF THE INVENTION

The present invention provides a method of operating a solid fuel fired boiler comprising introducing a solid fuel and an iron-bearing material into the boiler. The solid fuel is at least partially combusted in the boiler to produce an ash slag, wherein the ash fusion temperature characteristics (i.e., one or more of the IDT, ST, HT, and FT) of the ash slag are different than the ash fusion temperature characteristics of the ash slag that would result on combustion of the solid fuel alone. The method of the present invention is particularly applicable to slag tap boilers, including cyclone-type boilers. These boilers are, typically, designed to operate with a liquid ash slag.

The iron-bearing material may be, but is not limited to, at least one of iron ore beneficiation tailings, iron ore fines, pelletized blends of coal and iron-bearing material, pelletized solid fuel containing iron-bearing compounds, iron-bearing boiler ash, mill scale from steel production, dust from blast furnace gas cleaning equipment, flue dust from sinter plants, and other materials including iron or including material that bears iron. The iron-bearing material may be blended with the coal or other solid fuel that is to be fired in the boiler prior to or during combustion to modify one or more properties of the ash slag to meet the design specifications of the boiler. These properties may be, but are not limited to, ash fusion temperature characteristics, ash slag viscosity, ash slag base-to-acid ratio, as well as other properties.

According to the present invention, the iron-bearing material may be fed into the slag tap or other solid fuel fired boiler in one or more of several different locations. In pulverized fuel slag tap boilers, the material bearing iron compounds may be fed into, for example, the fuel pulverizers, the fuel transfer system, directly into the boilers, into the combustion chamber enclosure or any other location in the system. In cyclone slag tap boilers, the iron-bearing material may be fed into, for example, the fuel storage bunker, the fuel transfer system, the cyclone boilers directly, the combustion enclosure, or any other location in the system.

The method of the invention allows lower sulfur coals, as well as other fuels typically unsuited for use in slag top boilers, to be used in such boilers, significantly reducing SO_2 emissions.

The reader will appreciate the foregoing details and advantages of the present invention, as well as others, upon consideration of the following detailed description of embodiments of the invention. The reader also may comprehend such additional details and advantages of the present invention upon making and/or using the stainless steels of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

The features and advantages of the present invention may be better understood by reference to the accompanying drawings, in which:

FIG. 1 depicts a conventional coal-fired pulverized fuel slag tap boiler installation that may be modified to implement the method of the present invention;

FIG. 2 schematically depicts a conventional cyclone boiler installation that may be modified to implement the method of the present invention;

FIG. 3 is a graphical plot of temperature for 250-poise viscosity vs. base-to-acid ratio based on a ferric percentage of 20 utilized for estimating the T_{250} of a coal from the composition of the ash;

FIG. 4 schematically depicts a pulverized coal slag tap boiler installation and identifies several possible locations

for introduction of iron-bearing material into the boiler according to the method of the present invention; and

FIG. 5 depicts a cyclone boiler installation and identifies several possible locations for introduction of iron-bearing material into the boiler according to the method of the present invention.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

A conventional pulverized coal slag tap boiler is schematically depicted in FIG. 1 and is generally indicated as 10. Fuel may be fed to pulverizers 1, where the fuel is reduced in particle size. After pulverization, the fuel is transported, along with pulverizer gases, through fuel transfer system 2 to burners 3, where it is introduced to combustion chamber 5. In combustion chamber 5 the combustible portion of the fuel is largely consumed to produce heat, while the non-combustible portion of the fuel undergoes complex chemical transformations forming a fuel ash. The majority of the non-combustible portion of the fuel in a slag tap boiler should form ash slag in its liquid or molten state at the temperatures within the boiler. The solid portion of the fuel ash is generally called flue ash and should be entrained in the combustion gases.

Combustion chamber 5 of slag tap boiler 10 is enclosed, as is conventional, either partly or fully by heat transfer surface 7 which also is referred to as a waterwall. Waterwall 7 absorbs heat produced by combustion of the fuel in combustion chamber 5. Waterwall 7 typically contains a continuous feed of water which is converted to steam by heat generated in combustion chamber 5 for use in electric power generation or other uses.

The liquid or molten portion of the fuel ash in pulverized coal slag tap boiler 10 exits combustion chamber 5 through slag tap 6, while the remaining ash is entrained in combustion chamber gases fed to combustion chamber outlet 4. At combustion chamber outlet 4, the gases enter a passageway typically containing gas heat transfer surfaces 8 to recover the heat contained in the hot combustion chamber gases. In some cases a "slag screen" 9 may be mounted ahead of heat transfer surfaces 8, on which any ash particles entrained in the combustion gases may be collected and maintained in combustion chamber 5 as a slag. Slag screen 9 may reduce the potential deposition and fouling of heat transfer surfaces 8. Fouling of heat transfer surfaces 8 ultimately reduces the efficiency of boiler operation. If operation of the boiler becomes too inefficient, the boiler must be shut down and cleaned, which is costly, time-consuming, and takes the boiler out of service.

To maintain the necessary fuel ash slag flow from the slag tap 6 at the bottom of boiler 10, it is required that the AFT characteristics (i.e., IDT, ST, HT, and FT) of the ash be sufficiently low. In the case of boilers equipped with slag screens 9, it is also generally required that the AFT characteristics be sufficiently low as to prevent formation of slag screen deposits and screen pluggage, which would restrict the flow of combustion gases from combustion chamber 5.

Slag tap boilers are designed for the use of fuel with ash fusion temperatures below about 2600° F. Where fuel ash fusion temperatures are excessively high, the following operational difficulties may be encountered in the operation for slag tap boilers. First, ash slag with higher viscosity at combustion temperatures than the design viscosity of the boiler may result in poor ash flow properties under boiler operating conditions. This will stop slag flow out of the slag tap boiler and disrupt boiler operation. Second, the poor flow

properties of slag produced from ash having elevated fusion temperatures can produce buildup of slag in the combustion chamber, notably on heat transfer surfaces. This may result in reduced steam production by the boiler, as well as possible premature mechanical failure of boiler components. Third, where a slag screen 9 is installed, buildup of slag ash with poor flow properties on the screen can result in restrictions of the flow of combustion gases out of the boiler, causing reduction in steam production, and possibly a complete blockage of combustion gas flow.

The second category of slag tap boiler is the cyclone boiler system. A conventional cyclone furnace is shown schematically in FIG. 2 and is generally indicated as 11. Cyclone boiler 11 combusts a pulverized fuel to produce heat. Fuel is crushed in crusher 12A or 12B, typically so that approximately 95% of the fuel will pass through a 4-mesh screen. The fuel may be crushed to the desired particle size in crusher 12A prior to its introduction to the fuel storage bunker 13, or as it is fed from bunker 12B through transfer system 14. Cyclone boiler 11 has two water-cooled horizontal cylindrical cyclone burners 15 in which the fuel is fired and from which heat is released at extremely high rates. Approximately 20% of the combustion air enters burners 15 tangentially to impart a whirling motion to the incoming solid fuel. The remaining combustion air is admitted in the same direction tangentially at the roof of the cylinder of cyclone burners 15 and imparts further whirling or centrifugal action to the fuel particles. The operating temperature of combustion chamber 16 is typically designed to exceed 3000° F. (16500° C.). Coals are used in cyclone boilers that produce a liquid ash at these temperatures. The liquid ash forms a layer on the walls of cyclone burners 15. Some incoming coal particles are thrown to these walls by centrifugal forces, held in the slag, and scrubbed by the combustion air. Fuel and liquid slag are maintained in cyclone burners 15. Fuel is partially combusted in cyclone burners 15, and the balance of combustion is achieved as materials leave cyclone burners 15 and enter main combustion chamber 16, which is wholly of partly enclosed by waterwalls 17.

The molten slag in excess of the thin layer retained on waterwalls 17 continually drains away from the burner end of combustion chamber 16, discharges through slag tap 18 opening adjacent to lower cyclone burner 15, and is tapped into a slag tank, where the slag is solidified for disposal. The gaseous products of combustion are discharged into a gas-cooling portion of boiler 11. A portion or the fuel ash is entrained in the gaseous products and exits through combustion chamber outlet 19. Slag screen 20 may be mounted in this region to inhibit slag buildup on combustion gas heat exchange surfaces 21 due to entrained solids 11. Cyclone boilers are designed for fuels with low ash fusion temperatures (IDT, ST, HT, and FT) below about 2600° F. Where fuel with excessive ash fusion temperatures is used, the following operating difficulties can result. First, it may be difficult to maintain the flow of slag out of cyclone burners 15 and boiler slag tap 18. Second, slag buildup in main combustion chamber 16 may be difficult to remove from waterwalls 17, and this may result in mechanical failure of heat transfer surfaces 17 and 21.

Liquid coal ash can feasibly be removed from slag tap boilers if the slag ash has a viscosity of 250 poise or below at the operating temperature of the boiler. Slag tap boilers are typically designed for liquid coal ashes having a viscosity of 250 poise or less at 2600° F. Therefore, coals are usually classified by their T_{250}, which is the temperature in degrees Fahrenheit to obtain a 250 poise ash viscosity after combustion. The viscosity of coal fuel ash is typically

measured in a high temperature rotating-bob viscometer. The direct measurement of the viscosity of coal ash in this way at several temperatures provides reliable data that can be used to determine the suitability of various coals for use in slag tap type boilers. However, since the direct measurement of coal ash viscosity by a viscometer is a long and costly procedure, methods of estimating the coal ash viscosity or T_{250} from a chemical analysis of the coal ash have been developed.

Solid fuels, and particularly fossil fuels such as coal, used in steam generation may contain varying amounts of non-combustible constituents which, following the combustion process, are removed from the system in either a solid form, a liquid form, or both, as discussed above. Broadly, there are two sets of non-combustible chemical constituents of coal whose relative presence in the ash will influence AFT characteristics. These constituents of coal can be generally classified as either basic or acidic. The acidic constituents of coal typically are considered to be SiO_2, Al_2O_3, and TiO_2. The basic constituents typically are considered to be Fe_2O_3, CaO, MgO, Na_2O, and K_2O. Empirical studies have shown that the relative ratio of the basic to acidic constituents in the ash can be used to estimate the viscosity/temperature relationship of the fuel ash, including the silica ratio, the base-to-acid ratio, and the dolomite percentage. A higher ratio of basic constituents indicates lower AFT characteristics (i.e. lower IDT, ST, HT, and FT) of a fuel, and therefore, the basic constituents are considered to be the fluxes. The base-to-acid ratio is calculated by the following equation:

$$\text{Base-to-Acid Ratio} = \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

FIG. 3 is a plot of temperature for 250-poise viscosity vs. the base-to-acid ratio based on a ferric percentage of 20 utilized for estimating the T_{250} of a coal from the composition of the ash. The base-to-acid ratio is determined for an individual coal from the above equation, and the plot in FIG. 3 may be used to estimate the T_{250} of the coal and, therefore, its suitability for use in a slag tap boiler.

Fuels can also be considered to have bituminous-type ash or lignite-type ash. For bituminous-type ash the principle flux, or viscosity lowering, component is Fe_2O_3, while for lignite-type ash the principle fluxes are CaO and MgO, and some lignitic ashes may also contain elevated levels of Na_2O, and K_2O. Fuels with bituminous-type ash, which have low AFT characteristics due to elevated Fe_2O_3 contents, typically derive the iron oxides from pyrite in the fuel, and are also characterized by high pyretic sulfur contents and, hence, high sulfur dioxide emissions potential. Switching to lower sulfur fuels will cause fuel ash with lower iron contents and lower basicity to be produced in the furnace, resulting in the aforementioned slag and ash handling problems due to higher than design ash viscosity characteristics.

In one aspect, the present invention is directed to the addition of iron-bearing materials in conjunction with low sulfur solid fuels that would generally be considered unsuitable for combustion in a slag tap boiler to adjust the ash viscosity and AFT characteristics to meet the design characteristics for the boiler. In this way, stable boiler operation can be maintained while reducing sulfur dioxide emissions. Any iron-bearing bearing material may be added to the combustion process to adjust the ash viscosity characteristics. The iron-bearing material may be, for example, one or more of iron and iron oxide bearing materials such as, for

example, iron ore beneficiation tailings, iron ore fines, pelletized iron ore, pelletized blends of coal, other solid fuels including iron-bearing materials, iron-bearing boiler ash, mill scale from steel production, flue dust from blast furnace gas cleaning equipment, and flue dust from sinter plants. Other iron-bearing materials will be readily apparent to those of ordinary skill. The iron present in the iron-bearing materials may be in the form of ferric oxide (Fe_2O_3), ferrous oxide (FeO), or neutral iron (Fe), either alone of in combinations, as well as other chemical forms of iron. Typical iron ores that may be used to flux the fuel ash by the method of the present invention are hematite, taconite, and magnetite. Carbon may be present in the iron-bearing materials in the form of, for example, blast furnace flue dust, or carbon may be added to these materials to promote reduction of the iron oxides to more readily flux the fuel ash.

The one or more iron-bearing materials are added to the boiler in a ratio with the fuel to the boiler in order to produce a composite ash and slag chemistry that will resemble the design characteristics of the particular boiler. The iron-bearing materials may be added as furnished from the producer, or may be subject to further processing to optimize their use as fluxes. For example, the particle size distribution of the iron-bearing materials may be adjusted so that a certain fraction will be entrained in the combustion gas, and therefore, may be available to flux slag screen deposits, if necessary. Adjustment of the particle size distribution may be effected through agglomeration of particles or through size reduction of the particles, either alone or in combination to reduce the particle size distribution. Those of ordinary skill will be familiar with those and other methods of altering particle size distribution of solid materials.

The appropriate methods of introducing the iron-bearing material into the boiler will depend on the specific boiler design, installation, and boiler type. FIG. 4 depicts several locations for introducing iron-bearing material into a slag tap boiler. This figure is meant only as an example and not to limit the method of the present invention. The iron-bearing material may be fed from iron-bearing material storage 22 through transfer system 23 for introduction in slag tap boilers according to the method of the present invention at several locations including, but not limited to, the fuel transfer system 24, pulverizers 25, directly into burners 26, into combustion chamber enclosure 27, for example, through a lance inserted through an existing opening in the combustion chamber 27 enclosure, or at any other location in the system. FIG. 5 depicts several locations for introduction of the iron-bearing material into a cyclone boiler. Possible locations for introducing iron-bearing materials to flux the fuel ash in cyclone boilers include, but are not limited to, at iron-bearing material storage 28, through iron-bearing material transfer system 29, into the fuel storage bunker 30, into the fuel transfer system 31, directly into the cyclone boilers 32, into the combustion enclosure 33, for example, through a lance inserted through an existing opening in the combustion chamber 33 enclosure, or at any other location in the system.

In order to illustrate embodiments of the method of the present invention, Table 1 lists four different coals and typical properties of each coal type, including the composition of the resultant ash, AFT characteristics, and sulfur and iron contents. Fuels 1 and 2 are of a type commonly found in the midwestern United States region. These midwestern coals typical possess low AFT characteristics that render them suitable for use in slag tap boilers. Many slag tap boiler systems, in the United States and elsewhere, were originally designed to use fuels with the ash fusibility

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characteristics similar to fuels 1 and 2 of Table 1. Table 1 also indicates the United States Geological Survey (USGS) identification numbers for each coal listed.

Fuels 1 and 2 have significantly higher sulfur contents than fuels 3 and 4 listed in Table 1. The use of high sulfur coals may currently be precluded for combustion in many boilers based on current environmental regulations without installation of the equipment necessary to remove or scrub the resultant sulfur dioxide from the combustion gas. Fuels 3 and 4 and similar coals contain significantly lower concentrations of sulfur and may be suitable for use in coal fired boilers without expensive flue gas desulfurization equipment. However, the AFT characteristics of fuels 3 and 4 are above 2800° F. and therefore their use in a slag tap boiler would lead to slag handling problems as previously discussed. thus, fuels 3 and 4 are unsuitable for use in a slag tap boiler without suitable flue gas desulfurization equipment. Fuels 3 and 4 are typical of low sulfur content coal which also has high AFT characteristics. Fuels of this type may be rendered suitable for use in slag tap boilers by the method of the present invention. Addition of suitable amounts of iron-bearing material according to the method of the present invention to low sulfur coals with high AFT characteristics will adjust the base-to-acid ratio and ultimately the ash viscosity characteristics to render the low sulfur coals suitable for use in slag tap boilers. The addition of iron-bearing materials to low sulfur coals adjusts the iron content of the slag to more closely resemble that characteristic of the type of fuel represented in Table 1 by fuels 1 and 2.

TABLE 1

Analyses of Selected Fuels

Fuel	1	2	3	4
USGS I.D.#	219409	219414	195042	195040
Seam	Lower Kittanning	Pittsburgh	#2 Gas	#5 Block
County	Belmont	Belmont	Logan	Logan
State	Ohio	Ohio	West Virginia	West Virginia
Wt % Ash	13.8	8.9	11.1	10.2
Wt % Sulfur	5.2	3.8	0.60	0.60
Ash Analysis:				
Wt % SiO₂	43.0	34.0	59.0	56.0
Wt % Al₂O₃	4.8	21.0	29.0	27.0
Wt % CaO	2.8	2.9	0.84	3.6
Wt % MgO	0.13	0.71	0.50	0.50
Wt % Fe₂O₃	44.0	32.0	2.2	2.7
Wt % Fe	30.6	22.2	1.53	1.88
IDT (° F.)	1900	1980	2800+	2800+
ST (° F.)	1990	2080	2800+	2800+
FT (° F.)	2100	2150	2800+	2800+

In Table 2, chemical analyses of several iron-bearing materials are listed. These iron-bearing materials are listed only to provide an example of possible iron-bearing materials that maybe used in the method of the present invention. It is believed that other materials bearing iron may be used to adjust the ash viscosity characteristics according to the present invention, and the method of the present invention is not meant to be limited to the materials listed in Table 2. One of ordinary skill may, without undue experimentation, identify other useful iron-bearing materials. Iron-bearing materials listed in Table 2 include iron ore, taconite pellets, blast furnace flue dust, and blast furnace sludge. All of these materials contain a high concentration of iron, but also have low concentrations of materials that constitute the acidic constituents in fuel ash, for example, silicon or aluminum oxides. As such, addition of these materials to the combus-

tion chamber will have the relative effect of increasing the iron content of the slag produced from the fuel ash significantly over the acidic constituent, resulting in a reduction in AFT characteristics and T₂₅₀. The increase in iron content of slag accompanying the introduction of the iron-bearing materials to the slag will increase the base-to-acid ratio of the slag.

TABLE 2

Iron-bearing Materials

Number	1	2	3 Blast Furnace	4 Blast Furnace
Source	Taconite	Iron Ore	Flue Dust	B.F. Sludge
Wt % SiO₂	7.5	10.4	6.9	6.1
WT % Al₂O₃	0.64	1.5	2.5	3.0
Wt % CaO	0.36	0.36	3.1	2.7
Wt % MgO	0.47	0.01	0.7	0.7
Wt % Fe	61.1	50.4	32.2	28.6
Wt % C	—	—	38.5	40.8

The iron-bearing materials are preferably added to coal with high AFT characteristics in a quantity to adjust the composite slag viscosity characteristics to approximate that of a fuel with lower AFT characteristics for which the boiler was designed to operate. Those of ordinary skill may readily ascertain the necessary feed amount and feed rate of a particular iron-bearing material that must be used with a particular solid fuel. Typically, a coal-fired boiler is designed to operate with a coal from a specific region having certain properties, usually referred to as the "design fuel" of the boiler. There are several characteristics of the design coal that may be approximated in order to determine the quantity of iron-bearing material to add to the high AFT coal. These include but are not limited to the ash viscosity temperature characteristics of the design coal, the base-to-acid ratio of the design coal, and the iron content of the design coal.

An example of the method of the present invention is shown in Table 3. Fuel 2 of Table 3 is the design coal of the slag tap boiler of this example. Fuel 2 is a high sulfur coal with low AFT characteristics. Fuel 3 is a fuel that has high AFT characteristics and would be unsuitable for use in a slag tap boiler designed for fuel 2 without modification of the fuel's AFT characteristics. The base-to-acid ratio of fuels 2 and 3, listed in the Table 3, were calculated according to the equation listed above. In this equation the four sources of iron-bearing material listed in Table 2 will be blended with fuel 3 to adjust the AFT characteristics of the fuel to approximate the AFT characteristics of fuel 2. The blended fuels, fuels 3.1, 3.2, 3.3 and 3.4, have a target base-to-acid ratio of 0.65 to approximate the base-to-acid ratio of fuel 2. This method was used because the base-to-acid ratio of coal may be used to estimate the AFT characteristics and the ash viscosity of the ash slag. The amount of each of the iron-bearing materials required to approximate the design fuel may be determined with simple linear programming means utilizing the base-to-acid ratio equation, the base-to-acid ratio of the design fuel, and the base-to-acid ratio of the fuel to be adjusted. From this method the final ratio of the amount of the iron-bearing material and the fuel to be adjusted may be determined. This iron bearing material/fuel ratio was calculated for the four iron-bearing materials in Table 2 to blend with fuel 3 in Table 3 to approximate the AFT characteristics of fuel 2 in Table 3.

Addition rates required for the iron-bearing material may require further adjustment if additional iron-bearing material is desired to be entrained from the combustion chamber in

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the combustion gases to flux the slag on the slag screen or is lost in the flyash. It is envisioned that iron-bearing material addition rates as low as 0.50% and as high as 25% or more to the combustion chamber may be required, based on the ash properties of the fuel. Optimization of partitioning of the iron-bearing material to enter the boiler slag rather than the flyash, and research for each installation regarding the minimum base-to-acid ratio required for maintenance of acceptable slag flow properties will determine the final form and addition rate of the iron-bearing material.

TABLE 3

Examples of addition of iron-bearing materials					
Fuel	2	3	3.1	3.2	3.3	3.4
Addition Rates, wt % iron bearing material to fuel input rate.	0	0	7.1	9.1	13.5	15.5
Wt % SiO₂	34.0	59.0	38.9	37.1	38.6	37.0
Wt % Al₂O₃	21.0	29.0	17.9	16.6	18.3	18.2
Wt % CAO	2.9	0.84	0.64	0.62	2.6	2.5
Wt % MgO	0.71	0.50	0.49	0.28	0.8	0.81
W % Fe	22.2	1.53	24.8	23.6	23.3	22.7
base-to-acid ratio	0.64	0.04	0.65	0.65	0.65	0.65--

Accordingly, the present invention is directed to a method of modifying the operation of certain boiler types so that such boilers may utilize solid fuels otherwise unsuitable for use in the boilers. It is to be understood that the present description illustrates aspects of the invention relevant to a clear understanding of the invention. Certain aspects of the invention that would be apparent to those of ordinary skill in the art and that, therefore, would not facilitate a better understanding of the invention, have not been presented in order to simplify the present description. Although the present invention has been described in connection with certain embodiments, those embodiments should not be considered as limiting the true scope of the present invention. Those of ordinary skill in the art will, upon considering the foregoing description, recognize that modifications and variations of the invention may be employed. The foregoing description and the following claims are intended to cover all such variations and modifications of the invention.

We claim:

1. A method of operating a solid fuel fired boiler, comprising:

introducing a solid fuel into the boiler;

introducing an iron-bearing material into the boiler;

introducing at least one carbon compound along with the iron-bearing material, the at least one carbon compound promoting reduction of iron oxides; and

at least partially combusting the solid fuel to produce an ash slag, wherein at least one ash fusion temperature characteristic selected from the group consisting of initial deformation temperature, softening temperature, hemispherical temperature, and fluid temperature less than the same ash fusion temperature characteristic of a second ash slag produced from combustion of the solid fuel alone.

2. The method of claim 1, wherein the solid fuel comprises coal.

3. The method of claim 1, wherein the iron-bearing material is added to the solid fuel before introducing the solid fuel and the iron-bearing material into the boiler.

4. The method of claim 1, wherein the coal has a sulfur content less than 2% weight.

5. A method of operating a solid fuel fired boiler, comprising:

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introducing a solid fuel into a slag tap boiler;

introducing an iron-bearing material into the slag tap boiler, wherein the iron bearing material is at least one of iron ore beneficiation tailings, iron ore fines, pelletized blends of coal and iron-bearing material, pelletized solid fuel containing iron-bearing compounds, iron-bearing boiler ash, mill scale from steel production, dust from blast furnace gas cleaning equipment, and flue dust from sinter plants; and

at least partially combusting the solid fuel to produce an ash slag, wherein at least a portion of the iron bearing material fluxes the ash slag to produce a composite ash slag having at least one ash fusion temperature characteristic selected from the group consisting of initial deformation temperature, softening temperature, hemispherical temperature, and fluid temperature less than the same ash fusion temperature characteristic of the ash slag produced from combustion of the solid fuel alone.

6. The method of claim 5, wherein the solid fuel comprises coal.

7. The method of claim 5, wherein the composite ash slag has at least one ash fusion temperature characteristic selected from the group consisting of initial deformation temperature, softening temperature, hemispherical temperature, and fluid temperature less than 2600° F.

8. The method of claim 5, wherein the slag tap boiler is for at least one of steam production and electricity generation.

9. The method of claim 5, wherein the slag tap boiler is a cyclone boiler.

10. The method of claim 5, wherein the composite ash slag has a viscosity such that the composite ash slag flows from the slag tap boiler.

11. The method of claim 5, further comprising pulverizing the solid fuel prior to introducing the solid fuel into the slag tap boiler.

12. The method of claim 5, wherein the iron-bearing material is at least one material selected from the group consisting of iron ore beneficiation tailings, iron ore fines, pelletized iron ore, pelletized solid fuels containing at least one iron-bearing compound, iron-bearing boiler ash, mill scale from steel production, flue dust from blast furnace gas cleaning equipment, and flue dust from sinter plants.

13. The method of claim 5, wherein the iron-bearing material comprises at least one of ferric oxide, ferrous oxide, and neutral iron.

14. The method of claim 5, wherein the iron-bearing material comprises at least one of hematite, taconite, and magnetite.

15. The method of claim 5, wherein the iron-bearing material comprises at least one carbon compound.

16. The method of claim 5, further comprising introducing at least one carbon compound along with the iron-bearing material, the at least one carbon compound promoting reduction of iron oxides.

17. The method of claim 5, wherein the slag tap boiler comprises:

a pulverizer, wherein the solid fuel is fed to the pulverizer;

a burner;

a fuel transfer system communicating with the pulverizer and the burner; and

a combustion chamber comprising an enclosure at least partially surrounding the burner.

18. The method of claim 9, wherein the cyclone boiler comprises:

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a fuel storage bunker;

a cyclone burner;

a fuel transfer system communicating with the fuel storage bunker and the cyclone burner; and

a combustion chamber comprising an enclosure at least partially surrounding the burners.

19. The method of claim 5, wherein the concentration of iron-bearing material to solid fuel is from 1 to 25 weight percent of the total of the iron-bearing material and the solid fuel introduced into the slag tap boiler.

20. The method of claim 5, wherein the composite ash slag has a total iron concentration of 15 to 30 weight percent.

21. The method of claim 5, wherein the iron-bearing material is added to the solid fuel before introducing the solid fuel and the iron-bearing material into the slag tap boiler.

22. The method of claim 5, further comprising:

adjusting the particle size distribution of the iron-bearing material.

23. A method of operating a solid fuel fired boiler, comprising:

introducing a solid fuel into a cyclone boiler, wherein the cyclone boiler comprise:

a fuel storage bunker,

a cyclone burner,

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a fuel transfer system communicating with the fuel storage bunker and the cyclone burner, and

a combustion chamber comprising an enclosure at least partially surrounding the burner,

introducing an iron-bearing material into at least one of the fuel storage bunker, the fuel transfer system, the cyclone burner, and the combustion chamber, and

at least partially combusting the solid fuel to produce an ash slag, wherein at least one ash fusion temperature characteristic selected from the group consisting of initial deformation temperature, softening temperature, hemispherical temperature, and fluid temperature is less than the same ash fusion temperature characteristics of a second ash slag produced from combustion of the solid fuel alone.

24. The method of claim 23, wherein the iron-bearing material is introduced into the combustion chamber through a lance inserted through an opening in the combustion chamber enclosure.

25. The method of claim 23, wherein the solid fuel is a coal having a sulfur content less than 2% by weight.

26. The method of claim 6, wherein the coal comprises a sulfur content less than 2.0% by weight.

* * * * *

EXHIBIT 4

and K_2O. As discussed in the Refractories section of Chapter 5, the balance between the acidic and basic oxides in the ash is important in setting ash melting temperatures and in influencing corrosive attack of refractory (fluxing).

The *ash fusion temperature under oxidizing and reducing conditions* is another important test that provides very practical information. In this test (ASTM Standard D-1857), a sample of the material is ashed. The mineral ash is then pressed into a cone shape and placed in a muffle furnace on a tilted ceramic plate. The furnace temperature is ramped up at a set rate while the cone is observed. Four temperatures are noted:

> *Initial deformation temperature* (IDT), where the tip of the cone just shows deformation
>
> *Softening temperature* (ST), where the cone is slumped such that the height and width of the ash mass are equal
>
> *Hemispherical temperature* (HT), where the mass is fluid but, due to surface tension, has a hemispherical shape with the height equal to one-half of the width
>
> *Fluid temperature* (FT), where the molten ash viscosity is very low and the material flows down the plate with a thickness not greater than 1/16th in (0.15 cm).

In reducing atmospheres, the ST is often identified with the "fusion temperature" of the slag.

In combustors such as the fluid bed furnace that depend on maintaining "dry" (non-sticky) ash conditions, the IDT in the ash fusion temperature determination is a guide in setting the upper limit to the operating temperature. Similarly, the IDT is a useful guide in setting the maximum temperature where fly-ash laden furnace gases should enter a boiler-tube bank to avoid slag buildup on the tubes. For other furnaces and operating requirements, the fusion temperature is also useful both in the design and feasibility stage and in problem-solving situations.

The ash fusion test can be conducted under both oxidizing and reducing conditions. Both have utility in anticipating or understanding slag buildup problems. Although most combustors are oxidizing overall, almost any combustor has some oxygen-deficient zones. Such zones include the pyrolyzing/gasifying mass on refuse incinerator grates or sludge incinerator hearths and regions in other furnaces where the local air supply is overwhelmed by the available combustible matter. This can be very important since the fusion characteristics of ash can change dramatically as the environment shifts from oxidizing to reducing. This is particularly true for ashes containing large amounts of iron. The reduction of Fe_2O_3 to FeO involves a change in behavior of the iron oxide from an "acidic oxide" to a "basic oxide" that often leads to a lower initial deformation temperature.

A number of other useful *physical properties* may merit determination. These include melting point (to assess the potential for wastes to melt at incineration temperatures and run through openings in grates), viscosity (important in atomization of liquid wastes), and flash point (important in assessing safety problems and a key parameter in some regulatory definitions of "hazardous" combustible wastes).

Finally, the design of *materials handling* systems can benefit from data such as angle of repose (for bins and belt conveyors), particle size and density (for pneumatic conveyors), and the like.
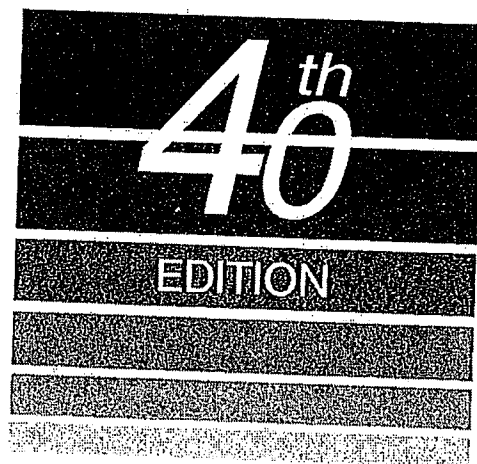
6. Regulatory/Process Definitions

Beyond the materials tests noted above, it may be appropriate to conduct several specialized tests or develop waste characterizations to make specific distinctions that

EXHIBIT 5

STEAM

its generation and use

4th

EDITION

Babcock & Wilcox
a McDermott company

Edited by S.C. Stultz and J.B. Kitto

This 40th edition is for the men and women who do the work of the world every day in power plants, paper mills, oil refineries, factories, and every other institution that uses a safety water tube boiler.

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Table 6
Properties of U.S. Coals

State	Anthracite	Pittsburgh #8 HV Bituminous	Illinois #6 HV Bituminous	Upper Freeport MV Bituminous	Spring Creek Subbituminous	Decker Subbituminous	Lignite	Lignite (S. Hallsville)	Lignite (Bryan)	Lignite (San Miguel)
	—	Ohio or Pa.	Illinois	Pennsylvania	Wyoming	Montana	North Dakota	Texas	Texas	Texas
Proximate:										
Moisture	7.7	5.2	17.6	2.2	24.1	23.4	33.3	37.7	34.1	14.2
Volatile matter, dry	6.4	40.2	44.2	28.1	43.1	40.8	43.6	45.2	31.5	21.2
Fixed carbon, dry	83.1	50.7	45.0	58.5	51.2	54.0	45.3	44.4	18.1	10.0
Ash, dry	10.5	9.1	10.8	13.4	5.7	5.2	11.1	10.4	50.4	68.8
Heating value, Btu/lb:										
As-received	11,890	12,540	10,300	12,970	9,190	9,540	7,090	7,080	3,930	2,740
Dry	12,880	13,230	12,500	13,260	12,110	12,450	10,630	11,360	5,960	3,200
MAF	14,390	14,550	14,010	15,320	12,840	13,130	11,960	12,680	12,020	10,260
Ultimate:										
Carbon	83.7	74.0	69.0	74.9	70.3	72.0	63.3	66.3	33.8	18.4
Hydrogen	1.9	5.1	4.9	4.7	5.0	5.0	4.5	4.9	3.3	2.3
Nitrogen	0.9	1.6	1.0	1.27	0.96	0.95	1.0	1.0	0.4	0.29
Sulfur	0.7	2.3	4.3	0.76	0.35	0.44	1.1	1.2	1.0	1.2
Ash	10.5	9.1	10.8	13.4	5.7	5.2	11.1	10.4	50.4	68.8
Oxygen	2.3	7.9	10.0	4.97	17.69	16.41	19.0	16.2	11.1	9.01

Ash fusion temps, F Reducing/Oxidizing:	Red	Oxid	Red	Oxid	Red	Oxid	Red	Oxid	Red	Oxid	Red	Oxid	Red	Oxid	Red	Oxid	Red	Oxid	Red	Oxid	Red	Oxid
ID	—	—	2220	2560	1930	2140	2750+	2750+	2100	2180	2120	2420	2030	2160	2000	2210	2370	2470	2730	2750+
ST Sp.	—	—	2440	2640	2040	2330	"	"	2160	2300	2250	2470	2130	2190	2060	2250	2580	2670	2750+	"
ST Hsp.	—	—	2470	2650	2080	2400	"	"	2170	2320	2270	2490	2170	2220	2090	2280	2690	2760	"	"
FT 0.0625 in.	—	—	2570	2670	2420	2600	"	"	2190	2360	2310	2510	2210	2280	2220	2350	2900+	2900+	"	"
FT Flat	—	—	2750+	2750+	2490	2700	"	"	2370	2700	2380	2750+	2300	2300	2330	2400	2900+	2900+	"	"

Ash analysis:										
SiO_2	51.0	50.58	41.68	59.60	32.61	23.77	29.80	23.32	62.4	66.85
Al_2O_3	34.0	24.62	20.0	27.42	13.38	15.79	10.0	13.0	21.5	23.62
Fe_2O_3	3.5	17.16	19.0	4.67	7.53	6.41	9.0	22.0	3.0	1.18
TiO_2	2.4	1.10	0.8	1.34	1.57	1.08	0.4	0.8	0.5	1.46
CaO	0.6	1.13	8.0	0.62	15.12	21.85	19.0	22.0	3.0	1.76
MgO	0.3	0.62	0.8	0.75	4.26	3.11	5.0	5.0	1.2	0.42
Na_2O	0.74	0.39	1.62	0.42	7.41	6.20	5.80	1.05	0.59	1.67
K_2O	2.65	1.99	1.63	2.47	0.87	0.57	0.49	0.27	0.92	1.57
P_2O_5	—	0.39	—	0.42	0.44	0.99	—	—	—	—
SO_3	1.38	1.11	4.41	0.99	14.56	18.85	20.85	9.08	3.50	1.32

Note: HV = high volatile; MV = medium volatile; ID = initial deformation temp; ST = softening temp; FT = fluid temp; Sp. = spherical; Hsp. = hemispherical.

mined outside the U.S. The source of this information, B&W's Fuels Catalogue, contains more than 10,000 fuel analyses performed and compiled since the 1950s.

Fuels derived from coal

Because of abundant supplies and low prices, the demand for coal as the prime or substitute fuel for utility boilers will most likely continue to increase. In addition, the future use of coal-derived fuels, such as coal refined liquids and gases, coal slurries, and chars, as inexpensive substitutes for oil and natural gas is also possible. Therefore, methods to obtain clean and efficiently burning fuels derived from coal are continually being investigated. A few of these fuels, which apply to steam generation, are discussed below.

Coke

When coal is heated in the absence of air or with a large deficiency of air, the lighter constituents are volatilized and the heavier hydrocarbons crack, liberating gases and tars and leaving a residue of carbon. Some of the volatilized portions crack on contact with the hot carbon, leaving an additional quantity of carbon. The carbonaceous residue containing the ash and some of the original coal sulfur is called coke. The amount of sulfur and ash in the coke mainly depends on the coal from which it is produced and the coking process used. The principal uses for coke are the production of pig iron in blast furnaces and the charging of iron foundry cupolas. Because it is smokeless when burned, considerable quantities have been used for space heating.

Undersized coke, called coke breeze, usually passing a 0.625 in. (15.875 mm) screen, is unsuitable for charging blast furnaces and is often used for steam generation. A typical analysis of coke breeze appears in Table 8. Approximately 4.5% of the coal supplied to slot type coke ovens is recovered as coke breeze. A portion of the coal tars produced as byproducts of the various coking processes may be burned in equipment similar to that used for heavy petroleum oil.